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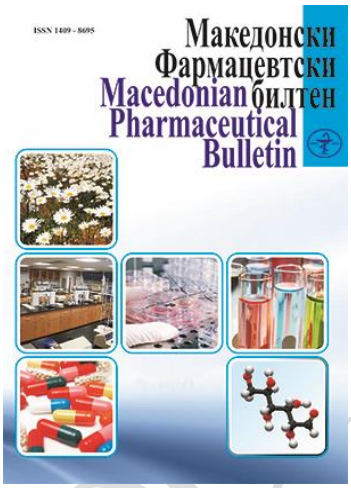

Title: Comparative evaluation of ICP-MS and GFAAS methods for determining lead and cadmium in food samples

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Comparative evaluation of ICP-MS and GFAAS methods for determining lead and cadmium in food samples

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Abstract

The determination of toxic potentially toxic elements in food is crucial for consumer health and regulatory monitoring. This study compared graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) for the quantification of lead (Pb) and cadmium (Cd) in fourteen food samples. Both methods demonstrated strong linearity ($R^2 \geq 0.998$) and met international validation criteria for precision, accuracy, and sensitivity. ICP-MS exhibited superior performance, with detection limits of 0.0008 µg/kg (Pb) and 0.0009 µg/kg (Cd) and RSD <1.2%, while GFAAS achieved LODs of 1.63 µg/kg (Pb) and 0.20 µg/kg (Cd) with RSD <2.3%. Recoveries ranged from 101.1% (Pb) to 98.1% (Cd) for GFAAS and were near 100% for ICP-MS. Analysis revealed variable metal concentrations: Cd ranged from 11.5 to 95.96 µg/kg, and Pb from 0.516 to 89.96 µg/kg, with the highest levels in peanuts, wheat, and potatoes. Paired t-tests indicated statistically significant differences ($p < 0.001$) between methods, with GFAAS slightly higher, but the deviations were minor (<2%) and did not affect practical interpretation or regulatory compliance. ICP-MS is recommended for ultratrace monitoring and regulatory purposes, whereas GFAAS provides a robust, accurate, and cost-effective approach for routine food analysis. All concentrations are expressed on a fresh weight basis.

Keywords: Lead, cadmium, food safety, potentially toxic elements, ICP-MS, GFAAS, method comparison

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Introduction

Potentially toxic elements (PTEs), such as lead (Pb) and cadmium (Cd), are persistent environmental contaminants with well-documented toxicological effects on human health (ATSDR, 2012; Jarup, 2003). Chronic exposure to these metals through dietary intake can result in severe health consequences, including neurotoxicity, renal dysfunction, impaired bone metabolism, and increased risk of cardiovascular diseases (EFSA, 2020; Godt et al., 2006; WHO, 2011).

Due to their non-biodegradable nature, Pb and Cd can persist in the environment and enter the food chain. However, their environmental behavior differs: Cd exhibits higher mobility and phytoavailability, whereas Pb generally remains strongly bound to soil particles and tends to accumulate mainly in plant roots with limited translocation to edible tissues. Therefore, continuous monitoring of Pb and Cd levels in commonly consumed foodstuffs is essential to ensure public safety and compliance with international regulatory standards established by EFSA and WHO/FAO (FAO/WHO, 2011; Heshmati et al., 2021).

The presence of Pb and Cd in foods can be influenced by multiple environmental and agricultural factors, including industrial emissions, contaminated irrigation water, the use of phosphate fertilizers, and soil geochemistry (Alloway, 2013; Sharma and Nagpal, 2020). Foods such as leafy vegetables, cereals, legumes, and fruits are recognized as common contributors to dietary exposure, making their analysis a key component of risk assessment programs (Satarug et al., 2010). Given the increasing global emphasis on food quality control, accurate quantification of potentially toxic elements (PTEs) is not only scientifically relevant but also crucial from a public-health standpoint.

Reliable determination of potentially toxic elements (PTEs) in complex food matrices requires analytical techniques that provide high sensitivity, precision, and accuracy. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are among the most widely employed techniques for this purpose. GFAAS is recognized for its cost-effectiveness, relatively simple instrumentation, and suitability for routine laboratory analysis, especially in facilities with limited resources; however, it has inherent limitations such as lower sample throughput, susceptibility to matrix effects, the need for matrix modifiers, and longer analysis time. (Welz and Sperling, 1999). In contrast, ICP-MS provides ultratrace detection limits, superior precision, rapid throughput,

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and the capability for multi-elemental analysis, making it the preferred choice for advanced monitoring programs. Nevertheless, ICP-MS operation requires high-purity reagents, controlled laboratory conditions, trained personnel, and higher operational costs (Hassan et al., 2022; Skoog et al., 2018; Thomas, 2013). Comparative evaluation of these techniques allows laboratories to balance analytical performance with operational efficiency and determine the most suitable approach for routine food-safety assessment.

The present study was undertaken to compare the analytical performance of GFAAS and ICP-MS for the determination of Pb and Cd in selected food samples, including fruits, vegetables, cereals, and legumes. Given the public-health risks associated with dietary exposure to these elements, accurate and reliable analytical techniques are essential for their monitoring in food.

Although ICP-MS typically provides substantially lower limits of detection and quantification (LOD/LOQ), both techniques can yield comparable accuracy when matrix effects are properly controlled and analytical conditions are optimized. Therefore, assessing their performance under identical conditions is important for determining their suitability for routine food-safety applications.

In addition to methodological comparison, this study examines the actual levels of Pb and Cd in a variety of commonly consumed foods. These concentrations are interpreted in relation to internationally established maximum levels (MLs) for toxic elements in food, such as those defined by the European Union and the Codex Alimentarius. By integrating method evaluation with regulatory context, the study aims to offer evidence-based recommendations that support laboratory method selection, regulatory decision-making, and improved consumer protection.

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Material and methods

Chemicals, reagents, and Materials

All solutions for the GFAAS measurements were prepared using ultrapure deionized water and stored in PP volumetric flasks to prevent trace-metal contamination. Prior to use, all laboratory plasticware and glassware were acid-washed by soaking for 24 h in a dilute nitric acid solution (1+9, *v/v*), prepared by diluting concentrated HNO_3 (≥65%) with ultrapure water. After acid treatment, all materials were thoroughly rinsed with distilled water and air-dried in a

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clean environment.

The reagents used in this study including nitric acid (65%) and hydrogen peroxide (30%) were of Suprapure grade (Merck, Darmstadt, Germany). Standard stock solutions of lead (Pb) and cadmium (Cd), each at a concentration of 1000 mg/L (Merck, Darmstadt, Germany), were employed for calibration. Daily working standards were freshly prepared by serial dilution of the stock solutions using 0.5% nitric acid.

Matrix Modifiers: For cadmium determination, a mixture of palladium nitrate ($Pd(NO_3)_2$, 10.0 g/L in 15% HNO_3) and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, 10 g/L in H_2O) was added, whereas for lead determination, ammonium dihydrogen phosphate ($NH_4H_2PO_4$, 100 g/L in 1% HNO_3) and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, 10 g/L in H_2O) were used. The concentrations of the modifiers in the final sample aliquot were controlled to ensure reproducibility. All reagents were obtained from CPA Chem, Bulgaria.

All reagents and chemicals used for the inductively coupled plasma mass spectrometry (ICP-MS) analysis were of analytical or trace metal grade. Ultrapure water (18.2 MΩ·cm) was produced using a Direct-Q 5UV purification system (Merck, Germany).

High-purity argon (99.999%) was used as the carrier gas for both GFAAS and ICP-MS measurements. Helium (99.999%) and hydrogen (99.999%) were available but were not employed in the present study, as no collision or reaction gases were required for the determination of Pb and Cd. All gases were supplied by Messer Technogas (Skopje, North Macedonia).

Multielement ICP-MS standard traceable to NIST containing 36 elements (10 mg/L each), as well as mercury referent standard (1000 mg/L) were obtained from Agilent Technologies, USA and CPA Chem, Bulgaria, respectively. Daily optimization of the instrument's settings was performed using ICP-MS tuning solution (containing Ba, Be, Ce, Co, In, Pb, Th, Tl, Mg in 2% HNO_3, 10 mg/L each). The tuning solution, 1 µg/kg was prepared before analysis using 1% HNO_3.

During all analytical procedures involving GFAAS and ICP-MS determinations, Grade A polymethylpentene (PMP) volumetric flasks and polypropylene (PP) tubes, together with beakers and graduated cylinders, were employed to minimize the risk of extraneous metal contamination. Prior to use, PP tubes were subjected to acid washing to reduce trace metal background levels, whereas PMP volumetric flasks were cleaned using laboratory-grade

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detergent and thoroughly rinsed with ultrapure water. Disposable pipettes were used exclusively for reagent additions in order to prevent cross-contamination.

Instrumentation

The determination of cadmium and lead concentrations was performed using graphite furnace atomic absorption spectrometry (GFAAS). Analytical conditions and measurement parameters were established according to the MKC EN 14083:2010 standard method (European Committee for Standardization, 2010), which was followed without any modifications.

An AAnalyst 600 atomic absorption spectrometer (PerkinElmer, USA) was utilized, equipped with a Transversely Heated Graphite Atomizer (THGA), Zeeman background correction, and an AS-800 autosampler for automated sample introduction. Element-specific hollow cathode lamps (HCL) were used as radiation sources for both Pb and Cd determinations.The instrument settings and analytical parameters used for Pb and Cd determinations are summarized in Table 1 and 2.

Table 1.

Table 2.

The instrument was operated under optimized furnace temperature programs to ensure maximum analyte sensitivity and minimal matrix interference (Table 3). Data acquisition and signal processing were performed using the WinLab 32 software package (PerkinElmer), which enabled automated calibration and background correction during analysis.

Table 3.

Microwave-assisted digestion of food samples prior to ICP-MS analysis was carried out using a Milestone Ethos Up system (Milestone Srl, Sorisole, Italy). The system was equipped with 15 high-pressure tetrafluoromethoxy polymer (TFM-PTFE) vessels (100 mL capacity), designed for uniform heat distribution and efficient digestion of organic matrices.

Quantitative elemental analysis was carried out using a PlasmaQuant MS Q quadrupole ICP-MS instrument (Analytik Jena, Germany). The instrument was equipped with a solid-state radiofrequency (RF) generator operating at 27 MHz, a quartz torch, and a concentric Micromist

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nebulizer, ensuring high sensitivity and stable performance for trace-level determination of Pb and Cd. Analytical conditions and measurement parameters were established in accordance with the MKC EN 17851:2023 standard method (European Committee for Standardization, 2023). Samples were introduced via a concentric Micromist glass nebulizer coupled to a Peltier-cooled Scott-type double-pass spray chamber. Argon was used as the plasma, auxiliary, and nebulizer gas. Ions were extracted through nickel sampler and skimmer cones and separated by a quadrupole mass analyzer. Detection was performed using an all-digital Adaptive Dynamic (AD) detector operated in pulse-counting mode. Plasma conditions and instrumental parameters are summarized in Table 4.

Table 4.

Daily optimization of ion optics, gas flow rates, and detector voltages was conducted to ensure analytical stability. Instrument control, data acquisition, and quantitative evaluation were performed using ASpect MS software (Analytik Jena).

Preparation of standard solutions

For the GFAAS determinations of lead and cadmium, three-point calibration curves were prepared from freshly diluted working standards. Lead (Pb) calibration standards were prepared at concentrations of 10, 20, and 30 µg/kg, while cadmium (Cd) standards were set at 1, 2, and 3 µg/kg. To achieve consistent atomization and ensure analytical precision, appropriate matrix modifiers were incorporated into all calibration standards at the same concentrations as used in the sample aliquots.

Primary stock solutions of Pb and Cd (1000 mg/L, Merck, Darmstadt, Germany) were used as the source standards. Working standards were prepared daily by serial dilution of the stock solutions using 0.5% (*v/v*) nitric acid, ensuring consistency and minimizing potential contamination. All solutions were prepared in PP volumetric flasks and stored in tightly sealed containers prior to analysis.

For ICP-MS analysis, calibration solutions were prepared by serial dilution of a certified Agilent multi-element ICP-MS standard solution, traceable to NIST, using 1% nitric acid (HNO_3) as the diluent. Intermediate stock solutions at concentrations of 100 µg/kg and 10 µg/kg

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were first prepared to facilitate accurate dilution and stability.

Nine calibration levels were used for the elements of interest (Cd and Pb) with final concentrations of 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 µg/kg in 1% HNO_3. Certified reference material (CRM) from the FAPAS proficiency testing program was used as quality control in this study Rice powder 07419.

Samples

A representative selection of commonly consumed food products was obtained from local retail markets or through official submissions by border health inspectors during January, February, March, and September 2025. The items were chosen based on their widespread consumption and availability. All products were either fresh, processed, or commercially packaged as appropriate. The samples were grouped as follows: fruits – kiwi, mandarin orange, lemon, orange, apple; vegetables – potato, potato puree, cabbage, beetroot; cereals – wheat, brown rice, white rice, popcorn; and legumes – peanut.

Sample preparation

For graphite furnace atomic absorption spectrometry (GFAAS), the samples were homogenized using an agate mortar and pestle to obtain a fine and uniform powder. The prepared material was stored in pre-cleaned polyethylene containers prior to digestion and subsequent analysis.

Approximately 300 mg of each homogenized sample was transferred into quartz microwave digestion vessels (Q80) and digested with concentrated nitric acid (65%) and hydrogen peroxide (30%) all of Suprapure quality. A reagent blank was prepared in parallel. Digestion was carried out using the Multiwave 3000 microwave system (Anton Paar, Austria) according to the manufacturer's recommended program. After cooling to room temperature, vessels were carefully opened under a fume hood, the inner walls rinsed with ultrapure deionized water, and the digests were quantitatively transferred to calibrated volumetric flasks, then diluted to a final volume of 20 mL. All solutions were clear and suitable for analysis.

For inductively coupled plasma mass spectrometry (ICP-MS), sample preparation followed the EN 13805:2015 standard (European Committee for Standardization, 2015). Approximately 0.3–0.5 g of each homogenized sample was weighed directly into TFM

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microwave vessels. To each sample, 3 mL of concentrated nitric acid (65%) and 1 mL of hydrogen peroxide (30%) were added. Blank solution containing only 3 mL HNO_3 65% and 1 mL H_2O_2 30% was also prepared. Microwave digestion was performed in two steps: an initial ramp to 200 °C over 15 minutes at 1600 W, followed by a holding step at 200 °C for an additional 15 minutes at the same power. After cooling, the digest was quantitatively transferred to 50 mL PP volumetric flasks and filled to volume with ultrapure deionized water. All samples were clear, and each sample was analyzed in triplicate using three independently prepared digests (n = 3).

Method validation

For the GFAAS technique, the reliability of the analytical procedure for the determination of lead and cadmium in food samples was confirmed through an internal method validation process performed in alignment with the ISO/IEC 17025:2012 standard. The evaluated parameters comprised linearity, sensitivity, limits of detection and quantification (LOD and LOQ), precision, and accuracy.

In the case of the ICP-MS method, validation was carried out in accordance with the ISO/IEC 17025:2012 quality assurance framework prior to the analysis of real food matrices and routine sample testing. The assessment included linearity, sensitivity, LOD, LOQ, precision, and accuracy.

Results and discussion

The analytical performance of graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) was evaluated through method validation and subsequent application to fourteen food samples (n = 14) with differing matrices and contamination levels of cadmium (Cd) and lead (Pb). All concentration results discussed herein are expressed on a fresh weight basis, in accordance with European Union (EU) maximum limit (ML) regulations for foodstuffs.

Both analytical techniques demonstrated excellent linearity within their respective calibration ranges, with coefficients of determination (R^2) exceeding 0.997 for GFAAS and 0.9999 for ICP-MS (Tables 5 and 6). The wider linear dynamic range of ICP-MS (0.5–200

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µg/kg) compared to GFAAS reflects the intrinsic advantages of mass spectrometric ion detection, which maintains proportionality over several orders of magnitude. In contrast, the narrower calibration ranges of GFAAS are consistent with the transient nature of atomization and absorption processes in electrothermal systems, which nonetheless provide reliable quantification within concentration ranges typically encountered in food analysis.

Precision studies revealed method-dependent variability. ICP-MS achieved relative standard deviation (RSD) values of approximately 1.00–1.13% for Pb and Cd, respectively (Table 6), reflecting stable plasma conditions and highly reproducible ion counting. GFAAS exhibited slightly higher but still acceptable RSD values (1.79–2.25%) (Table 5), which can be attributed to the pulsed measurement mode of graphite furnace atomization, as well as sensitivity to matrix composition, modifier efficiency, and furnace temperature gradients. Nevertheless, the precision of both techniques comfortably meets internationally accepted analytical performance criteria.

Table 5.

Table 6.

Accuracy, evaluated via recovery experiments using certified reference materials, further confirmed the reliability of both methods. Recoveries ranged from 98.1% to 101.1% for GFAAS and from 99.4% to 101.0% for ICP-MS (Table 7), with low associated RSD values (<1.5%). The slightly higher recoveries observed for GFAAS may be attributed to matrix-induced signal enhancement, a known phenomenon in electrothermal AAS when analyzing organic-rich digests. In contrast, ICP-MS recoveries were very close to unity, reflecting its reduced susceptibility to matrix effects under optimized plasma conditions.

Table 7.

Despite their strong performance, both techniques present inherent limitations that should be considered. GFAAS measurements may be affected by matrix interferences, furnace memory effects, and edge effects within the graphite tube, particularly when analyzing complex food matrices. These factors can contribute to increased variability and require careful

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optimization of temperature programs and matrix modifiers.

ICP-MS, while offering superior sensitivity and multi-elemental capability, may be influenced by spectral interferences arising from polyatomic ions and matrix-induced signal suppression or enhancement. However, such effects are substantially minimized through optimized plasma conditions and appropriate instrument tuning. The markedly lower limits of detection achieved by ICP-MS (LOD ≈ 0.0008–0.0009 µg/kg) compared to GFAAS (LOD ≈ 0.2–1.6 µg/kg) highlight its clear advantage for ultra-trace analysis, particularly in fruits and food products with inherently low metal concentrations.

Accordingly, ICP-MS is particularly suited for regulatory monitoring and research applications requiring ultra-trace quantification, whereas GFAAS remains a robust, cost-effective, and sufficiently accurate method for routine analysis in laboratories with limited resources.

The analysis of fourteen food samples revealed notable variability in Cd and Pb concentrations depending on food type (Tables 8 and 9; Figures 1 and 2). For Pb, the highest concentrations were observed in potato samples, ranging from approximately 60.0 to 90.0 µg/kg (fresh weight) by ICP-MS and from 61.3 to 91.8 µg/kg by GFAAS. This finding is consistent with the known tendency of tuber crops to accumulate Pb from contaminated soils, particularly in regions with historical agricultural or industrial activities.

Table 8.

Table 9.

Figure 1.

Figure 2.

In contrast, fruits such as apple, kiwi, orange, and mandarin exhibited substantially lower Pb concentrations (<5 µg/kg), reflecting the limited translocation of Pb from roots to fruit tissues. Cadmium concentrations followed a different distribution pattern, with the highest levels detected in peanuts (≈96 µg/kg) and wheat (≈88 µg/kg). Fruits generally showed lower Cd concentrations (11–32 µg/kg); however, these values are relatively elevated compared to typical background levels. This observation may be explained by cultivar-specific uptake characteristics, soil pH, organic matter content, and localized environmental conditions, all of

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which can significantly influence Cd bioavailability and soil-to-plant transfer.

When evaluated within the regulatory framework of Commission Regulation (EU) 2023/915 (European Commission, 2023), all analyzed samples complied with the applicable EU maximum levels. Cd concentrations in peanuts approached but did not exceed the EU ML for nuts (100 µg/kg fresh weight), warranting attention due to cadmium's cumulative toxicity and long biological half-life. Pb concentrations in all samples remained well below EU MLs for the respective food categories; nevertheless, the comparatively higher Pb levels observed in potatoes emphasize the importance of continued monitoring, particularly given the well-documented neurotoxicity of lead, especially in children.

To assess agreement between GFAAS and ICP-MS, a paired t-test was applied to Cd and Pb concentration data obtained from the fourteen paired samples (n = 14). The statistical analysis demonstrated that GFAAS produced higher concentrations than ICP-MS for both metals (Table 10). The mean difference (± SD) between methods was 0.83±0.23 µg/kg for Pb and 1.15±0.45 µg/kg for Cd, with corresponding t-values indicating statistically significant differences ($p < 0.001$).

Table 10.

Although statistically significant, these differences were small in relative terms (<2%) and therefore do not materially affect the interpretation of contamination levels or regulatory compliance. This highlights an important distinction between statistical significance and practical significance, confirming that both techniques provide analytically comparable results within the concentration ranges relevant for food safety assessment.

Overall, both GFAAS and ICP-MS demonstrated strong analytical performance for the determination of Cd and Pb in diverse food matrices. ICP-MS offers superior sensitivity, precision, and multi-element capability, making it the preferred technique for ultra-trace analysis and regulatory surveillance. GFAAS, while less sensitive and characterized by a narrower linear range, remains a reliable and economically viable option for routine screening and analysis of moderately contaminated food samples. Within food safety analytical frameworks, the two techniques should be regarded as complementary, with method selection guided by laboratory infrastructure, target concentration levels, and regulatory requirements.

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Conclusion

This study confirms that both inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) are suitable for the determination of cadmium (Cd) and lead (Pb) in fourteen food matrices (n = 14), with results expressed on a fresh weight basis in line with EU regulatory requirements. Both methods met validation criteria for linearity, precision, accuracy, and sensitivity.

ICP-MS showed superior analytical performance, providing a wide linear range (0.5–200 µg/kg), very low detection and quantification limits, and excellent precision (RSD ≈ 1.00–1.13%), which supports its use for ultra-trace analysis and regulatory monitoring. GFAAS exhibited higher detection limits (LOD: 0.20–1.63 µg/kg) but maintained acceptable precision (RSD: 1.79–2.25%) and accuracy, with recoveries close to 100%, confirming its suitability for routine food analysis.

Analysis of real samples revealed variability in Cd and Pb concentrations depending on food type, with higher Cd levels in peanuts and cereals and higher Pb levels in potatoes. All measured concentrations were below EU maximum limits, although some values approached regulatory thresholds, emphasizing the need for continued monitoring.

Statistical comparison showed significant differences between the two methods ($p < 0.001$); however, these differences were minor (<2%) and did not affect regulatory compliance or interpretation of results. Overall, ICP-MS is recommended for ultra-trace determination, while GFAAS remains a reliable and cost-effective alternative for routine food safety monitoring. The complementary use of both techniques provides a flexible and robust approach for food safety monitoring.

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Резиме

Компаративна аналитичка евалуација на методите ICP-MS и GFAAS за квантитативно одредување на олово и кадмиум во храна

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Клучни зборови: олово, кадмиум, безбедност на храна, потенцијално токсични елементи, ICP-MS, GFAAS, споредба на методи

Одредувањето на токсични потенцијално опасни елементи во храна е од клучно значење за заштита на здравјето на потрошувачите и за регулаторен надзор. Во оваа студија се споредија GFAAS и ICP-MS за квантитативно определување на олово (Pb) и кадмиум (Cd) во четиринаесет примероци на храна. Двете методи покажаа висока линеарност ($R^2 \geq 0.998$) и ги исполнија меѓународните критериуми за валидирање во однос на прецизност, точност и сензитивност. ICP-MS демонстрираше супериорни аналитички перформанси, со граници на детекција 0.0008 µg/kg (Pb) и 0.0009 µg/kg (Cd) и RSD <1.2%, додека GFAAS постигна LOD од 1.63 µg/kg (Pb) и 0.20 µg/kg (Cd) со RSD <2.3%. Вратливостите се движеше од 101.1% (Pb) до 98.1% (Cd) за GFAAS и беа приближно 100% за ICP-MS. Анализата покажа варијабилност во концентрациите на металите: Cd се движеше од 11.5 до 95.96 µg/kg, а Pb од 0.516 до 89.96 µg/kg, при што највисоки вредности беа забележани во кикирики, пченица и компири. Парни t-тестови укажаа на статистички значајни разлики ($p < 0.001$) помеѓу методите, при што GFAAS даваше малку повисоки вредности, но отклонувањата беа минимални (<2%) и не влијаеја на практичната интерпретација или усогласеност со регулативата. ICP-MS се препорачува за ултратрасно следење и регулаторни цели, додека GFAAS нуди робустен, точен и

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економичен пристап за рутинска анализа на храна. Сите концентрации се изразени на основа на свежа маса.

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Table 1. Operating parameters for Pb determination by GFAAS (THGA, PerkinElmer AAnalyst 600)

Wavelength (nm)	283.3	Ashing Temp. (°C)	850
Slit Width (nm)	0.7	Atomization Temp. (°C)	1500
Tube/Platform Type	Pyro/Platform	Rollover (A)	
Matrix modifier	0.050 mg $NH_4H_2PO_4$ + 0.003 mg $Mg(NO_3)_2$		
Characteristic Mass	30.0 pg/0.0044 A·s		
Sensitivity Test Concentration	50.0 μg/L for 0.13 A·s		

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Table 2. Operating parameters for Cd determination by GFAAS (THGA, PerkinElmer AAnalyst 600

Wavelength (nm)	228.8	Ashing Temp. (°C)	700
Slit Width (nm)	0.7	Atomization Temp. (°C)	1400
Tube/Platform Type	Pyro/Platform	Rollover (A):	0.8
Matrix modifier	0.050 mg $NH_4H_2PO_4$ + 0.003 mg $Mg(NO_3)_2$		
Characteristic Mass	1.3 pg/0.0044 A·s		
Sensitivity Test Concentration	2.0 μg/L for 0.15 A·s		

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Table 3. Furnace program for conditioning a graphite tube

Step	Temperature (°C)	Ramp (s)	Hold Time (s)	Argon Gas Flow (mL/min)
Dry 1	110	1	20	250
Dry 2	130	5	30	250
Pyrolysis	850	10	20	250
Atomize	1600	0	5	0
Clean-out	2450	1	2	250

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Table 4. Operating parameters for ICP-MS analysis (PlasmaQuant MS Q, Analytik Jena)

Spray chamber	Scott type double pass glass
Nebulizer	MicroMist concentric glass nebulizer
RF power (W)	1300
Plasma gas flow (Ar, L/min)	7.5-10.5
Nebulizer gas flow (Ar, L/min)	0.8
Sample uptake rate (mL/min)	0.4
Scan mode	Peak hopping
Resolution (m/Δm)	0.8
Replicate time (s)	9.78
Dwell time (ms)	50
Sweeps/reading	20
Integration time (ms)	1000
Replicates	3

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Table 5. Validation parameters for lead (Pb) and cadmium (Cd) determination by GFAAS

Parameter	GFAAS (Pb)	GFAAS (Cd)
Calibration range (µg/kg)	10–30	1–3
Linearity (R^2)	0.9984	0.9970
LOD (µg/kg)	1.63	0.20
LOQ (µg/kg)	3.26	0.40
Intercept	-0.00031	0.00345
Slope	0.00097	0.03938
Precision (RSD, %)	1.79	2.25
Accuracy (recovery, %)	101.1	98.1

*All concentrations are expressed in µg/kg . RSD calculated from 3 determinations. LOD and LOQ were calculated as 3σ and 10σ of procedural blanks.

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Table 6. Validation parameters for cadmium (Cd) and lead (Pb) determination by ICP-MS

Parameter	ICP-MS (Pb)	ICP-MS (Cd)
Calibration range (µg/kg)	0.5–200	0.5–200
Linearity (R^2)	0.9999	0.9999
LOD (µg/kg)	0.0008	0.0009
LOQ (µg/kg)	0.0028	0.0029
Intercept (c/s)	5110.7	61.3
Slope (c/s)	787700	79330
Precision (RSD, %)	1.00	1.13

*All concentrations are expressed in µg/kg. RSD calculated from 3 determinations. LOD and LOQ were calculated as 3σ and 10σ of procedural blanks.

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Table 7. Results obtained for method's accuracy and precision using CRM 07419 (Rice powder)

Element	Assigned value (μg/kg)	Amount found (μg/kg)	Recovery (%)	RSD (%)
Cd	96.00	96.95±1.27	100.98	1.31
Pb	291.00	289.00±3.23	99.36	1.12

*Results are expressed as mean ±SD

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Table 8. Lead (Pb) concentrations in selected food samples

Sample	ICP-MS Pb (µg/kg) ± SD	GFAAS Pb (µg/kg) ± SD
Apple	1.31 ± 0.01	1.33 ± 0.03
Beetroot	16.56 ± 0.17	16.60 ± 0.33
Brown rice	2.10 ± 0.02	2.12 ± 0.04
Cabbage	7.74 ± 0.07	7.78 ± 0.16
Kiwi	1.96 ± 0.02	1.98 ± 0.04
Lemon	0.51 ± 0.005	0.53 ± 0.01
Mandarin orange	4.70 ± 0.04	4.74 ± 0.09
Orange	1.42 ± 0.01	1.45 ± 0.03
Peanut	8.84 ± 0.08	8.90 ± 0.18
Popcorn	8.03 ± 0.08	8.10 ± 0.16
Potato	89.96 ± 0.90	90.10 ± 1.80
Potato puree	60.04 ± 0.60	60.06 ± 1.20
Wheat	25.91 ± 0.26	26.00 ± 0.52
White rice	48.17 ± 0.48	48.30 ± 0.97

* Values are mean ± SD of three replicate measurements. Concentrations reported on a fresh weight basis.

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Table 9. Cadmium (Cd) concentrations in selected food samples

Sample	ICP-MS Cd (µg/kg) ± SD	GFAAS Cd (µg/kg) ± SD
Apple	18.12 ± 0.20	18.20 ± 0.40
Beetroot	11.50 ± 0.13	11.60 ± 0.26
Brown rice	29.16 ± 0.32	29.30 ± 0.64
Cabbage	22.22 ± 0.24	22.40 ± 0.49
Kiwi	13.25 ± 0.15	13.35 ± 0.29
Lemon	28.05 ± 0.31	28.20 ± 0.62
Mandarin orange	84.28 ± 0.93	84.50 ± 1.86
Orange	31.53 ± 0.35	31.70 ± 0.70
Peanut	95.96 ± 1.06	96.20 ± 2.12
Popcorn	21.44 ± 0.24	21.60 ± 0.47
Potato	67.93 ± 0.75	68.10 ± 1.50
Potato puree	55.36 ± 0.61	55.50 ± 1.22
Wheat	88.30 ± 0.97	88.60 ± 1.95
White rice	20.28 ± 0.22	20.40 ± 0.45

* Values are mean ± SD of three replicate measurements. Concentrations reported on a fresh weight basis.

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Table 10. Paired t-test comparison of Pb and Cd concentrations determined by ICP-MS and GFAAS

Element	Mean Difference (GFAAS − ICP-MS, µg/kg)	SD of Difference	t-value	Df	p-value	Remarks/ Interpretation
Pb	0.05	0.04	4.7	13	0.0004	A statistically significant difference was observed; GFAAS yielded higher Pb concentrations than ICP-MS
Cd	0.17	0.14	4.5	13	0.0006	A statistically significant difference was observed; GFAAS yielded higher Cd concentrations than ICP-MS

*p-values were calculated using a two-tailed paired t-test. The standard deviation (SD) of the differences was derived from three independent replicate measurements (n = 3). All concentrations are expressed on a fresh weight basis, unless otherwise stated.

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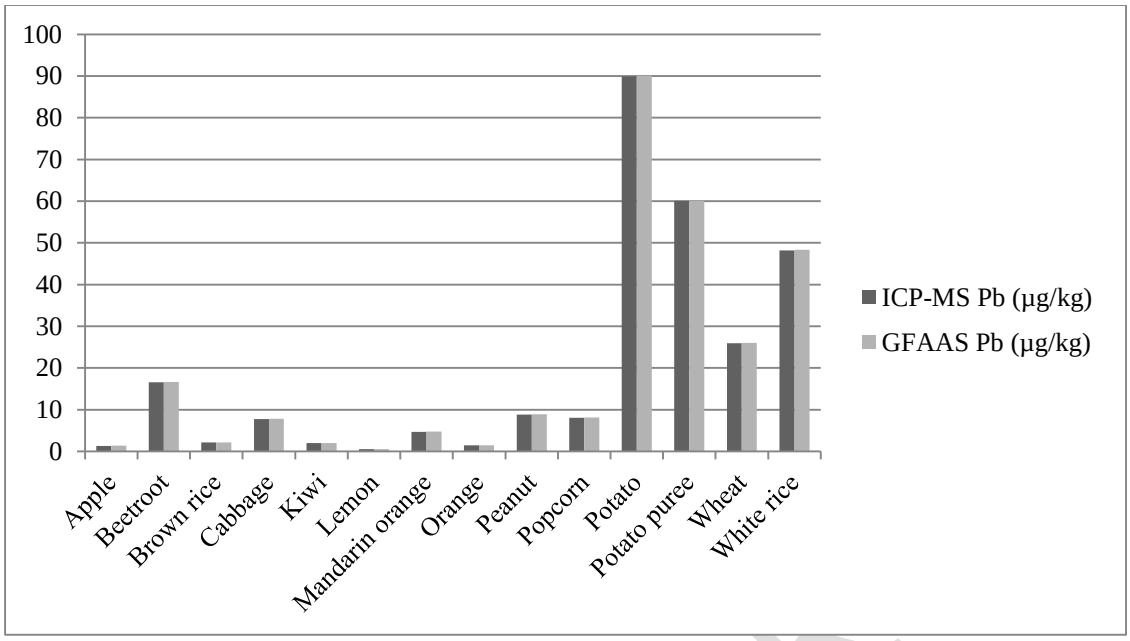

Fig. 1. Graphical representation of Pb concentrations measured in food samples.

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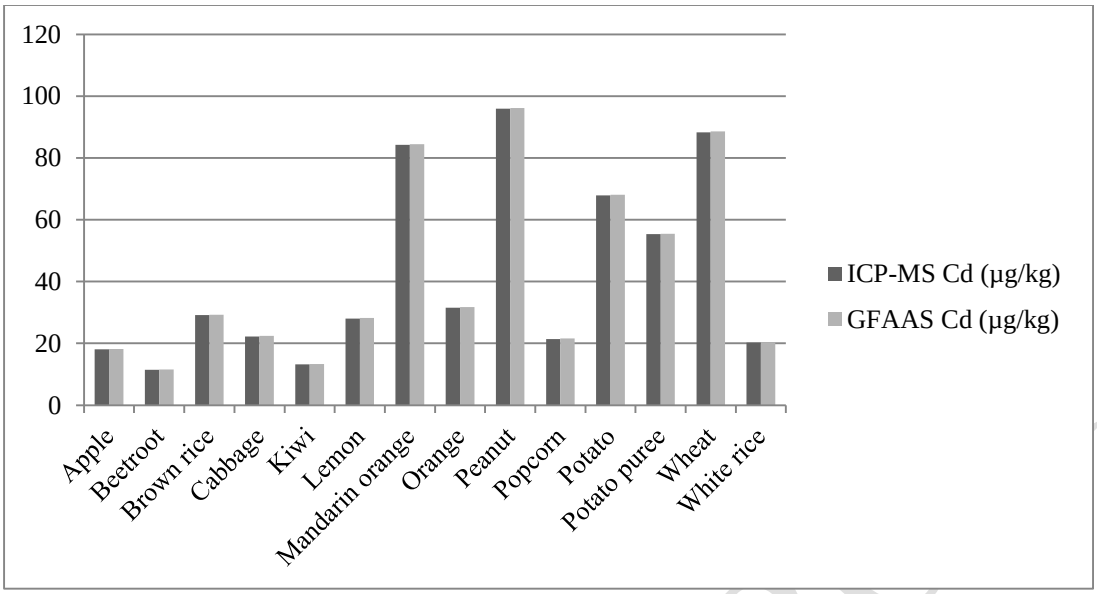

Fig. 2. Graphical representation of Cd concentrations measured in food samples.

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