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Heavy metal toxins in breakfast cereals – a baseline study using hybrid plasma mass spectrometry

Abstract

Plasma mass spectrometry is renowned for its high performance and impeccable capability and is a valuable asset for ultra-trace analysis of heavy metals. Heavy metal contamination of foodstuff is hazardous to human health and necessitates stringent analytical procedures to accurately evaluate toxic levels in samples. Our research team undertook investigation of the levels of arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) in eight brands of breakfast cereals as an initiative to provide guidelines for such elements in cereals. Inductively coupled plasma mass spectrometry (ICP-MS) was employed to detect concentrations of the toxins under study. The technique is one of the foremost in trace analysis and the capability of the instrument was validated by the use of certified reference standards. Minor aberrations in performance were monitored by the use of internal standards. Linearity, background correction and the removal of interferences were attained by deployment of sophisticated software. The argon flow associated with the plasma torch was 14.0L/min. Cereal samples were digested in ultrapure nitric acid, diluted in mild aqueous media (1% HNO_3) and subjected to ICP-MS analysis. The elements under study produced appreciable levels in most samples: Arsenic: 100-900µg/L; cadmium: 8-50µg/L; mercury: 270-370µg/L; lead: 115-30000µg/L. These values were compared with EU permissible levels in general foodstuffs and were found to be within the acceptable limit, except for Pb, which displayed elevated levels up to a factor of 5 in some samples. Our study makes a definite contribution to sustainable living and would be of interest to food safety organizations

Keywords: plasma mass spectrometry, cereals, toxic trace metals, ICP-MS

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Introduction

Breakfast cereals are made for public consumption and are widely popular all over the world, especially with children. Cereals are derived from plants, therefore, trace metal contamination of the cereal itself has its origin in the vegetable matter from which it is produced.[1] Heavy metals[2,3] could also infiltrate foodstuff from the equipment that is deployed to process them. However, some toxic elements such as mercury and arsenic, for example, are unlikely to be found at appreciable levels in equipment, thus, any form of contamination could mainly originate from environmental sources.[4] Growth of plants linked to cereals depends on certain agricultural conditions and if these conditions lend themselves to pollution, elemental uptake in the plant could result in elevated metal toxins. Contaminated soil conditioners, polluted irrigation water and noxious pesticides could all play a role in contaminating vegetable matter that are associated with cereal production. Our investigation is, therefore, an environmental study and any remedial measures for minimising trace metals in cereals should seriously consider remediating environmental factors associated with plant-based foodstuff.

This study employed hyphenated plasma mass spectrometry (ICP-MS) for assessing elemental profiles of the toxic metals of interest. ICP-MS is particularly well known for its high senstiivity and excellent detection limits. It surpasses other contemporary techniques such as X-ray fluorescence (XRF), Proton Induced X-ray Emission (PIXE), Electro Thermal Atomic Absorption (ETAA), Neutron Activation Analysis (NAA). Many of these current techniques possess certain drawbacks[5–13] that tend to make them unsuitable for ultra-trace analysis. For example, XRF requires prolonged sample preparation and is not well suited to liquid analysis. PIXE is useful mainly for solids and surface analysis. ETAA is beset by matrix interferences; and NAA fails if radioactive products from analytes have ultra-short half-lives. However, ICP-MS is multi-elemental, rapid, and highly facile.[14–17] The heavy metals under study in this work were: arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb). It is important to emphasise that our research makes a definite contribution to sustainable living by providing data that could be considered a guideline for heavy elemental profiles in breakfast cereals. Creating an environment that is more sustainable will undoubtedly be of immense global benefit.[18,19]

Materials and methods

Instrumentation/sample treatment

Cereals of different brands were purchased from local retail outlets in the United Arab Emirates (UAE). The samples were digested and diluted in aqueous acidic media (1% HNO_3) and transferred to special vials for ICP-MS analysis. Each sample solution was aspirated into the instrument via a nebulizer unit and conveyed to hot argon plasma (6000-8000K) where it was converted to ions, characteristic of the elements of interest, which were subsequently transmitted to a mass spectrometer for detection. The ICP-MS depicted in Figure 1 is a Perkin Elmer DRC-e instrument, manufactured in Canada, by Perkin Elmer. The instrument was equipped with a Scot spray chamber as part of the sample introduction system. Two high-vacuum diaphragm pumps and a turbo molecular pump in tandem provided the required ultra-high vacuum (~2.2×10^{-6} Torr) within the mass spectrometer region. The instrument also possesses a collision/reaction cell to ward off matrix related interferences and to form polyatomic combinations, as the analysis demanded. Collision/reaction gas flow was adjusted by a separate mass flow controller, which could be independently regulated and monitored. Data derived from spectral measurements were accumulated and recorded, and numerical analysis was undertaken by verifying sample data against suitable certified standards. Updated software was employed to detect sample interferences and matrix effects. Minor perturbations in instrumental drift and discernable fluctuations in performance were regulated by the use of suitable internal standards. Instrument calibration and correction for unwanted noise was accomplished by the use of reference standards. The nebulizer gas flow in the system was 0.80L/min. Prior to sample analysis the performance of the instrument was validated for repeatability.

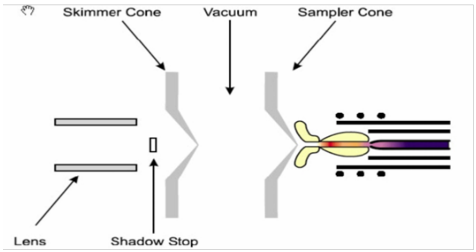

Figure 1 The ICP-MS for highly discrete mass separation.

Results and discussion

Repeatability

The instrument was initially calibrated using certified calibration standards (Perkin Elmer multi-element calibration standard N9300231). Following the standard calibration procedure, the mass spectrometer performance was checked using certified reference standards (Fluka 70007) to determine the uniformity of measurements and to assess the capacity of the technique in attaining the prescribed detection limits. The numerical performance of the method was confirmed by making measurements in triplicate (n=3) for each sample and standard. The instrument operates by introducing three separate sample aliquots into the plasma in rapid succession and the software subsequently computes the standard deviation. If the measured relative standard deviation (RSD) exceeds 10% the sample is re-analyzed to ascertain whether matrix effects or other instrumental factors are affecting the results. For our purposes RSDs <5% were satisfactory. Based on the results displayed in Table 1, it was evident that the mass spectrometer was working at its optimum accuracy and precision. In addition the detection limits of the instrument were checked and established using certified detection limit solutions.

Table 1 Repeatability study using a multi-elemental aqueous standard (Fluka 70007)

Quality control runs (10µg/L standard, Perkin Elmer QC2-1)					
Element	Trial 1	Trial 2	Trial 3	Mean	Mean ± SD%
Vanadium	9.51	9.74	9.90	9.67	9.67 ± 1.97
Chromium	9.82	9.61	9.39	9.66	9.66 ± 2.13
Manganese	9.46	9.72	9.39	9.51	9.51 ± 1.53
Cobalt	10.21	10.09	9.34	9.96	9.96 ± 4.20
Nickel	9.59	9.79	8.96	9.48	9.48 ± 3.81
Arsenic	10.01	9.42	9.29	9.69	9.69 ± 4.03
Selenium	9.78	9.36	9.28	9.55	9.55 ± 2.80
Molybdenum	10.01	10.14	10.44	10.40	10.40 ± 4.28
Cadmium	9.51	10.06	9.82	9.73	9.73 ± 2.74
Thallium	9.59	9.65	10.57	9.85	9.85 ± 4.88
Thorium	10.54	10.68	11.36	10.78	10.78 ± 3.64
Uranium	10.08	9.65	10.12	9.98	9.98 ± 2.23

Profiles of metal toxins

At the outset, it is important to emphasize that our work forms a significant contribution to sustainability.[18] Sustainable development embraces all activities that contribute to beneficial human health. The cereal samples investigated here were prepared by directly subjecting them to the digestion procedure, followed by immediate analysis. The elemental profiles of the metals of interest appear in Figures 2-5. From observation of these data it is evident that there is wide scatter among the results for each of the metals studied. This scatter could be attributed to a variety of factors which are discussed below.

Arsenic (As): The permissible limit of arsenic in solid foods is 1400ppb.[20] Our results reveal that the As concentrations detected in the samples of interest were well within the maximum admissible limit. The highest value recorded was for sample #7: >800ppb. The remaining samples delineated concentrations in the range 100-180ppb. The biological effects of As are well known. At toxic levels this element attacks the kidneys and liver with symptomatic effects of convulsions and severe abdominal pains.[21,22] As mentioned earlier cereals are universally consumed as breakfast foods by children. Even moderate to medium high levels of As could have a cumulative effect on minors who have sensitive organs. The origin of this element in cereals could be found in environmental sources. Clearly, from the plot in Figure 2 the fluctuation in concentrations of this element is wide, suggesting that the samples originated from diverse environmental sources.

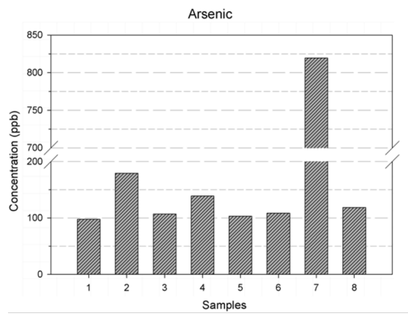

Figure 2 Arsenic concentrations in cereal samples.

Cadmium (Cd): The acceptable limit of cadmium in cereals is 100ppb.[20] The experimentally determined results (Figure 3) depict a range of about 10-60ppb, which is well within the international limit. The health effects of elevated levels of Cd are quite severe and are linked to disorders relating to renal failure and bone damage.[23] Humans ingest cadmium through plant-based foods. Such foods could

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be treated for de-metallization, which would be highly beneficial to human health. The undulating range of concentrations reflected in Figure 3 again demonstrate that environments and growing conditions that spawn the plants associated with these breakfast cereals are essentially responsible for the origin of trace and toxic metals.

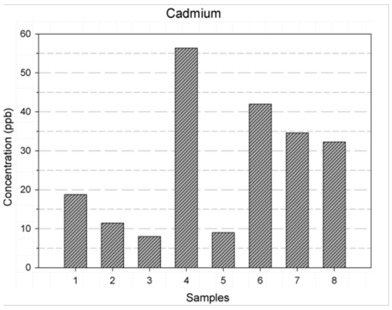

Figure 3 Cadmium concentrations in cereal samples.

Mercury (Hg): It is common knowledge that mercury compounds are highly hazardous at toxic levels. The maximum permissible level in foodstuff is 500ppb.[20] Our samples have a range of about 250-400ppb (Figure 4). Although this range is below the toxicity level of mercury, daily consumption of cereal could lead to bioaccumulation of this metal. It is known that such toxins could accumulate in tissue and organs; therefore, continued intake could lead to peripheral disorders. Children, especially, could be affected simply because their organs are tender and in the developmental stage.[24] Mercury poisoning tends to affect the muscles and general bodily coordination. It was surprising to find that the recorded results were at such appreciable levels, even though below the permissible limit. This suggests that the plant-based origins of these cereals are susceptible to uptake of this toxin.

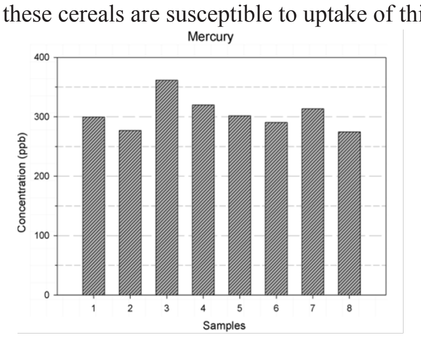

Figure 4 Mercury concentrations in cereal samples.

Lead (Pb): Lead has been acknowledged to be responsible for neurotoxic disorders in children.[25] The international limit for lead in foodstuff is 6000ppb.[20] The data in Figure 5 show that in light of this value sample #6 and #7 are elevated: >10000 and 30000ppb, respectively. The abnormally high level in sample #7 is surprising as it is 5 times higher than the international acceptable limit. This is a cause for concern simply because breakfast cereals are consumed on a daily basis and elevated levels could be potentially hazardous for children. De-metallization treatment of this element is recommended for those cereals that display elevated levels. Such treatment could commence with the soil and water used to nurture the plants associated with the production of these cereals. It should be emphasized that in the interest of sustainable development remedial measures should be adopted to curb the level of this element in breakfast cereals.

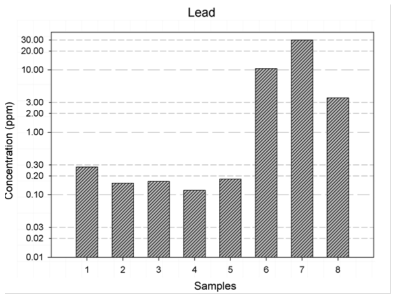

Figure 5 Lead concentrations in cereal samples.

Impact of the study

The images appearing in Figures 2-5 clearly demonstrate the variability of the data, which could possibly be deployed in "fingerprinting" exercises to identify the origin of each cereal. For example the Hg/Cd ratio in sample #3 or the Pb/Cd ratio in sample #7 could be used to provenance their region or country of origin. This "provenancing" or mapping study could be extended by applying more sophisticated algorithms to the data. Clearly, the data shown in this study could be useful to health and nutrition organizations and indicate that regular quality control is vital for the production and sale of wholesome foods. Of the four toxic metals studied, only lead showed elevated levels in two samples. In one sample (#7) we found that it was particularly elevated by more than 5 times the permissible limit. Such levels could have originated from two possible sources: (i) instrumental error; and (ii) environmental conditions. Instrumental error could be ruled out, as repeatability of each sample is constantly monitored. What remains are environmental factors associated with pollution: soil, irrigation water, manure and pesticides. There is no doubt that these factors play a key role in all plant-derived foodstuffs and it is usually elements of the environment that are culpable for elevated levels of toxins. There are two possible strategies to adopt to minimize the hazard: (i) intensive quality control; (ii) de-contamination of the environment. Both strategies would involve certain remedial measures such as possible chemical treatment of soil and water prior to use for agricultural purposes. Remedial measures are imperative as breakfast cereals are in use all over the world; such measures would also play a major role in contributing to sustainable living.

Conclusion

Our research focused on the elemental profiles of arsenic, cadmium, mercury and lead in different breakfast cereals, and could be considered a benchmark study. The experimentally determined results showed that Pb was observed at elevated levels in two samples. This could entail a hazard because Pb is responsible for neurotoxic disorders in children. Since breakfast cereals are consumed globally certain remedial measures should be put in place to minimize such toxicity. An extension to this study could involve evaluation of other potential toxins such as chromium, antimony and tin. These metals could be toxic to human cells even at low concentrations. Besides, antimony is a suspected carcinogen by current standards.

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Conflict of interest

The author declares that there is no conflict of interest.

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