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DETECTION OF LOW LEVEL ACTINIDES (Th, U) AND BISMUTH IN BREAKFAST CEREALS: A BASELINE STUDY

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ABSTRACT

Benchmarking the composition of bismuth (Bi), thorium (Th) and uranium (U) in breakfast cereals has not been previously documented and could be considered a baseline study in this domain of research. Detection of naturally occurring actinides is generally below the lower limit of detection in most contemporary methods of analysis. However, hyphenated plasma mass spectrometry (ICP-MS) has the capability of achieving a limit of detection in the ng/L (ppt) range and is, therefore, favorable for investigating levels of noxious metals at ultra-low levels in foodstuffs. Bismuth, thorium and uranium rarely occur at appreciable levels in most foodstuffs and their detection would be a useful contribution to knowledge related to nutrients. For the metals of interest we detected the following range of concentrations in breakfast cereals: Bi: 3-14 µg/L; Th: 6-100 µg/L and U: 1-15 µg/L. The elemental profiles of these metals are discussed and the feasibility of employing the data for fingerprinting studies is reported. There are no well-known toxicological guidelines for these elements and their health effects form part of ongoing studies in clinical research. Our study could make a significant contribution to sustainability and current nutritional research.

Keywords: ICP-MS, uranium, thorium, bismuth, cereals.

INTRODUCTION

Of considerable significance is that our study makes a contribution to sustainable living (Jarvis *et al*., 1992; Robinson *et al*., 2014). Detection of Bi, Th and U has evaded several contemporary techniques (Murray, 2010) simply because these trace heavy metals lie below the level of detection of many such techniques (Abbu *et al*., 2000; Al-Kindy *et al*., 2009; Peisach *et al*., 1994a; Peisach *et al*., 1994b; Pillay and Peisach, 1992; Pillay and Peisach, 1994; Pillay *et al*., 2005; Salih *et al*., 2005). Our work on the detection of these low-level actinides in breakfast cereals has not been previously reported in the existing published literature and from this perspective the study is seminal. The data produced in this paper therefore, constitutes a baseline study. Without doubt, the detection of Bi, Th and U in foodstuffs is a challenging initiative, not without analytical difficulties. However, ICP-MS is renowned for its superiority (Elkadi *et al*., 2010; Elkadi *et al*., 2014; Elkadi *et al*., 2013; Pillay *et al*., 2010; Pillay *et al*., 2014) in this respect and its sensitivity surpasses many current analytical methods. Luminescence methods, neutron activation, fluorescence techniques and charged particle activation are not particularly useful as they are not adequately sensitive.

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Sustainable living and sustainable development are related to the welfare of the world's population and to studies that benefit society as a whole (Robinson, 1993). Determination of the levels of noxious metals in foodstuffs is linked to nutrition and nourishment and the resulting health effects of these contaminants. Toxicology of the elements under study, Bi, Th and U, is of wide interest largely because their hazards to humans remain relatively unknown. Constant medical research is underway to evaluate the biological effects of these rare pollutants (Dupree *et al*., 1995). Breakfast cereals are consumed globally and our work on the profiles of bismuth and low level actinides, thorium and uranium, will also supplement knowledge derived from clinical research.

MATERIALS AND METHODS

Instrumentation / Sample Treatment

Eight different brands of cereal were obtained from local stores. Samples were treated in moderate aqueous acidic media (1% HNO_3), digested, and transferred to individual vials for ICP-MS investigation. Each sample solution was introduced to the instrument via an aspirator, nebulized into a fine spray of droplets, and transported to a high-temperature argon plasma (6000-8000 K), where it is ionized, and conveyed to a high-performance mass spectrometer for analysis. A schematic of the core of the ICP-MS is illustrated in Figure 1. The facility is furnished with a quadrupole mass filter consisting of four molybdenum rods, positioned diametrically opposite each other. The opposite pairs of rods are supplied with AC and DC voltages, which are rapidly switched in combination with an RF field (Jenner *et al*., 1990; Williams *et al*., 2012). This results in a sequentially changing electrostatic field, which allows only ions of a single mass-to-charge ratio (m/e) to pass through the filter at a given instant in time. The switching process and the mass selection process are sequential, and occur at a very rapid rate so that the quadrupole mass filter can separate up to 2400 amu (atomic mass units) per second. Acquisition of data depends on various features, and elaborate software is deployed to de-convolute sample interferences and matrix effects. Mild aberrations in instrumental performance were modulated by internal standards. Reference standards were deployed for determination of linearity and calibration. The nebulizer gas flow in the instrument was 0.80 L/min. The instrument was automated for repeatability measurements.

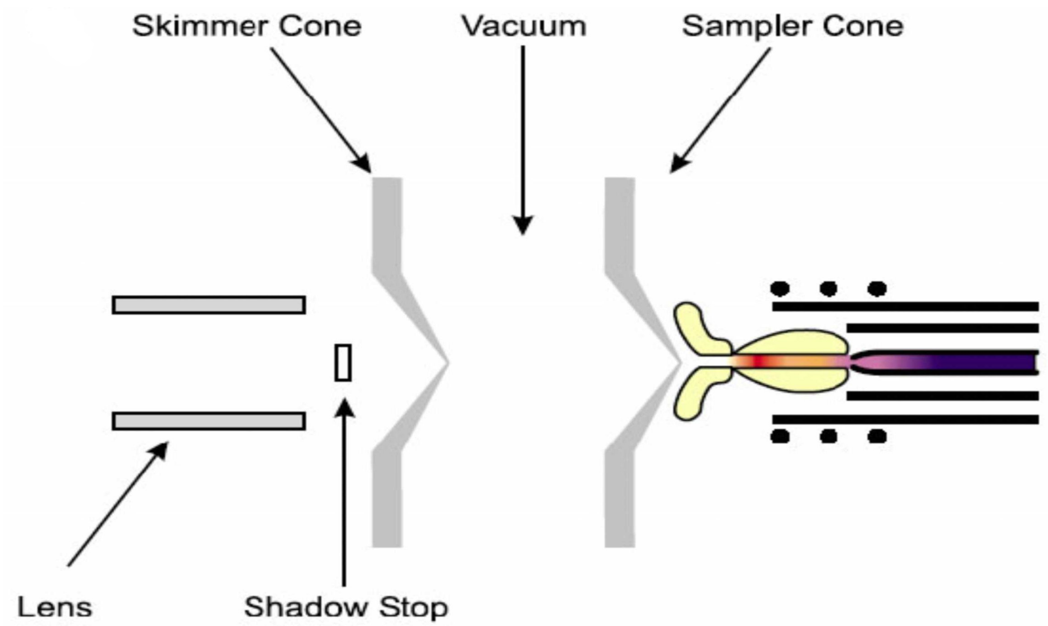

Fig. 1. Schematic of the core of the ICP-MS.

RESULTS AND DISCUSSION

Standardization/Repeatability

Calibration of the instrument was achieved with certified standards. Linearity of the system was established using licensed reference standards (Fluka 70007). Validation of data was substantiated by iterative measurements in triplicate (n=3) for each sample. The instrument functioned by aspirating three individual sample fractions into the plasma at rapid intervals and programming the software system to compute relative standard deviations RSD). If the measured relative RSD exceeds 10%, due to undesirable interferences or minor perturbations in the operational performance of the facility, the iterative analysis of the sample is reset and the procedure restarts. Iterative analyses of this nature ensured the integrity of the experimental results. Our work required RSDs within 5%, which were considered satisfactory. The data displayed in Table 1, demonstrate that the repeatability of the instrument was excellent. The detector itself was cross-calibrated using certified solutions.

Table 1. Repeatability study (µg/L) using a multi-elemental aqueous standard (Fluka 70007).

Measurement	Be	Mg	Co	Ni	In	Ce	Bi
1	10.6	10.5	9.9	9.9	9.6	9.7	9.0
2	10.5	10.5	10.5	10.2	9.5	9.2	9.5
3	10.8	10.7	9.9	10.1	9.7	9.0	9.2
Mean ± RSD	10.6 ± 0.9%	10.6 ± 1.7%	10.1 ± 4.0%	10.0 ± 1.0%	9.6 ± 0.6%	9.4 ± 4.0%	9.2± 3.1%

Elemental profiles of bismuth and actinides

Breakfast cereals are globally consumed and are a favourite with children. These cereals are plant-based, therefore, it is easy to deduce that any contamination of the cereal itself could have its origin in the plant from which it was produced. Plants such as corn, wheat, barley and rice are used to make cereals and these plants are often grown under conditions that could lend themselves to elevated uptake of metals. Some heavy metals could enter processed foods from the equipment and machinery that produces them. However, it is unlikely to find bismuth and actinides as contaminants at significant levels in equipment. Hence the inference is that any such pollutants could originate mainly from the environment. Contamination of plant-based cereals is linked to certain farming conditions, which could result in abnormal uptake of metal toxins. The kinetics of such uptake probably varies for different metals and for differing agricultural conditions. Therefore, scatter in the experimentally determined results is expected. Items associated with natural environment such as soil conditioners, irrigation water and pesticides could contaminate the plants that are linked to cereal production. This investigation is, thus a study in sustainability and a certain level of remediation could be considered for limiting metal toxins in cereals.

Bismuth (Z=83): the average natural abundance of bismuth is about 2 x 10^{-5}%. It is therefore, unlikely that appreciable concentrations of Bi are expected to be found in foodstuffs. It has been reported that the occurrence of Bi in some foods, like dairy products and fish, is roughly 1 ppb. Its level in drinking water is about 10 ppb. The experimental results for Bi in breakfast cereals appear in Figure 2. The data reflect that the concentrations of Bi in some cereals exceed 13 ppb – more than 13 times higher than the levels occurring in fish and dairy products. The range of Bi levels is between 3-14 ppb. Clearly, there is evidence in our data that these levels are elevated, and the reason for this elevation is not clear. As mentioned earlier, the origin of bismuth linked to plant-based foods is the soil and irrigation water. If these agricultural sources are contaminated it is likely that the uptake in plants, from which the cereals are derived, could be responsible for the unusually raised levels of bismuth. The variability of the data in Figure 2 reflect the variability in the respective environments associated with the cereals.

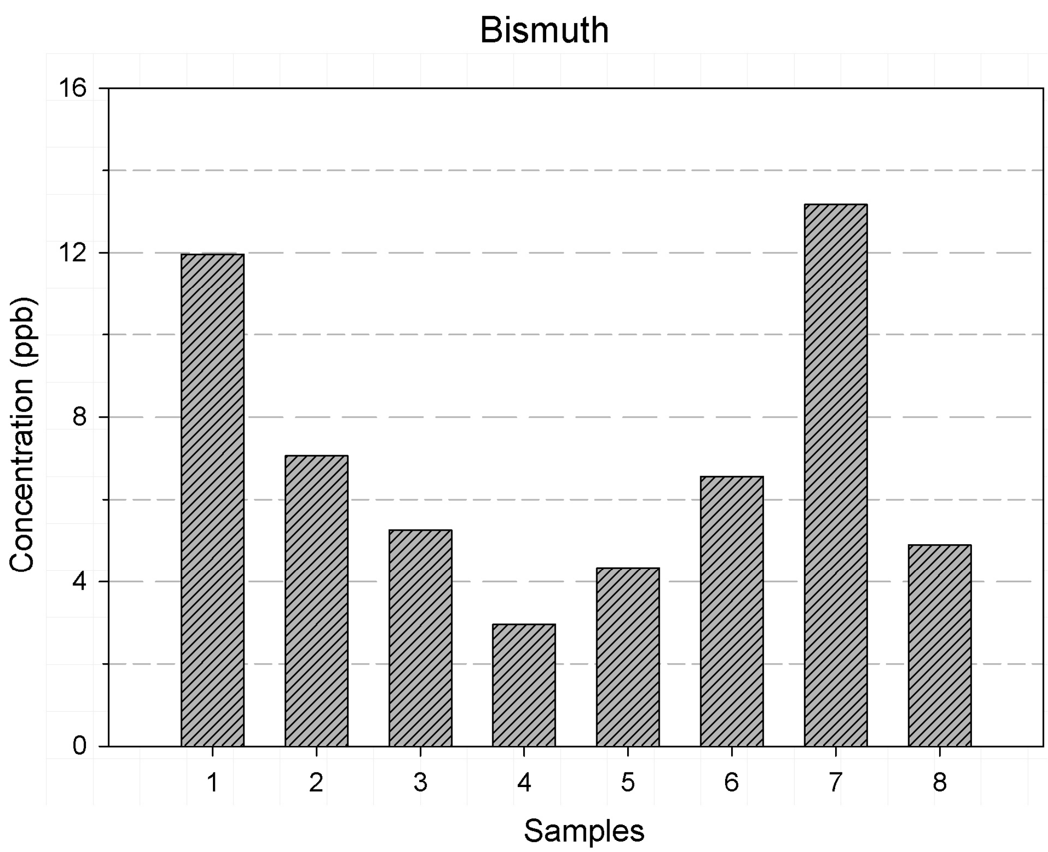

Fig. 2. Bismuth levels in cereals.

Thorium (Z=90): Thorium is found in soils at trace levels, roughly 6 ppm. About 99% of this element exists in the form of ^{232}Th. Thorium enters the body through water and soil. In the case of breakfast cereals the thorium content comes from uptake in the plant (wheat, barley, corn) used to prepare the breakfast cereal. There have been limited clinical studies on thorium and the results of health effects emerging from these studies show that lung disease and cancer are associated with elevated intakes of thorium. The data in Figure 3 represent the experimentally recorded results from the breakfast cereals under study. The concentrations of thorium ranged between 6-97 ppb. The wide scatter in these results reflects the appreciable variability in the environmental conditions linked to these cereals. Sample#1 depicted the highest level, close to 100 ppb. It is difficult to say whether this level is abnormally high or not because there are no distinct guidelines in the literature. However, the Th concentration in sample#1 is roughly 16 times higher than sample#8, suggesting the adoption of remedial measures to reduce Th in this breakfast cereal.

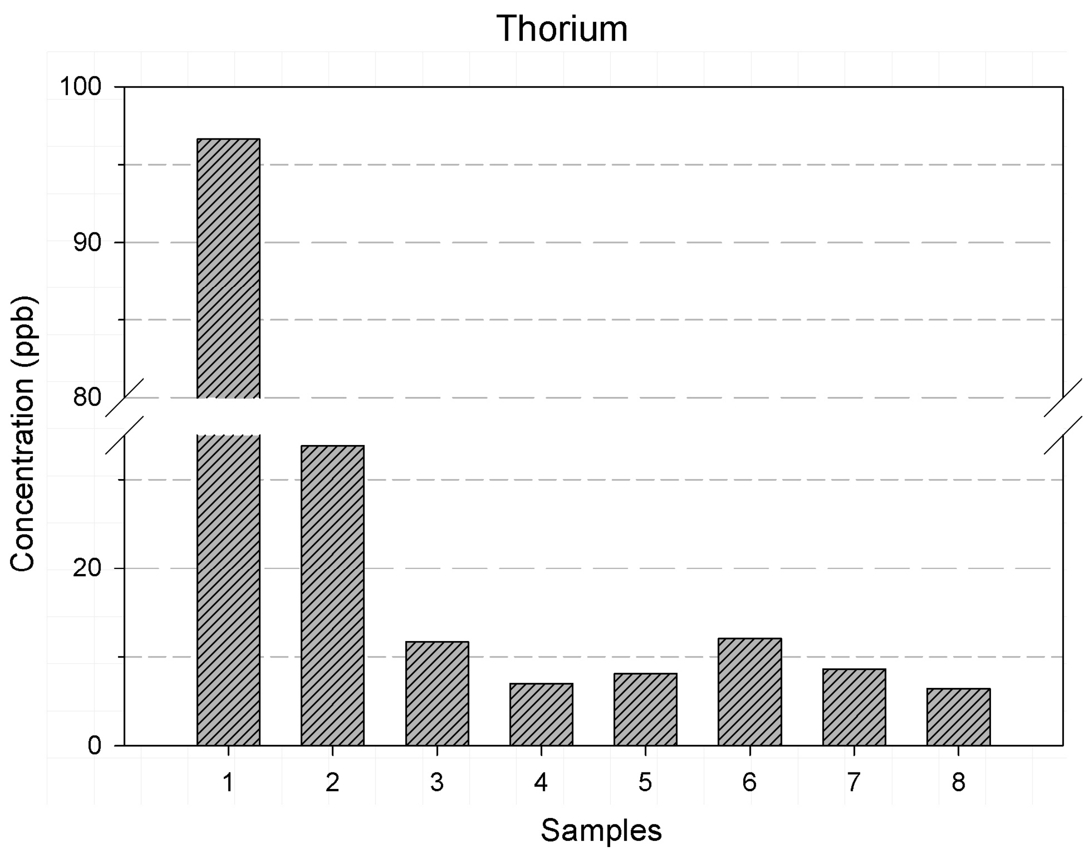

Fig. 3. Thorium levels in cereals.

Uranium (Z=92): Uranium occurs naturally in the environment and its composition is a mixture of isotopes: 99.3%, ^{238}U; 0.71%, ^{235}U; and 0.005, ^{234}U. Uranium, like bismuth and thorium infiltrate foods mainly through soil and water. Soil usually contains about 3 ppm uranium. Intake from uranium is roughly 1 µg/day. Plants cultivated near uranium mines are expected to possess higher levels of uranium. Most of the uranium is stored in the root of the plant. Another source of uranium is aerosols containing uranium hexafluoride and uranium trioxide. Toxicity of uranium results in renal disorders and also affects the reproductive system. Pulmonary disorders have also been reported in some clinical studies. The data in Figure 4 reveal that the range in U levels is 3-13 ppb. This range is similar to that of Bi, suggesting that these two elements experience similar uptakes in vegetation associated with breakfast cereals (barley, wheat, corn).

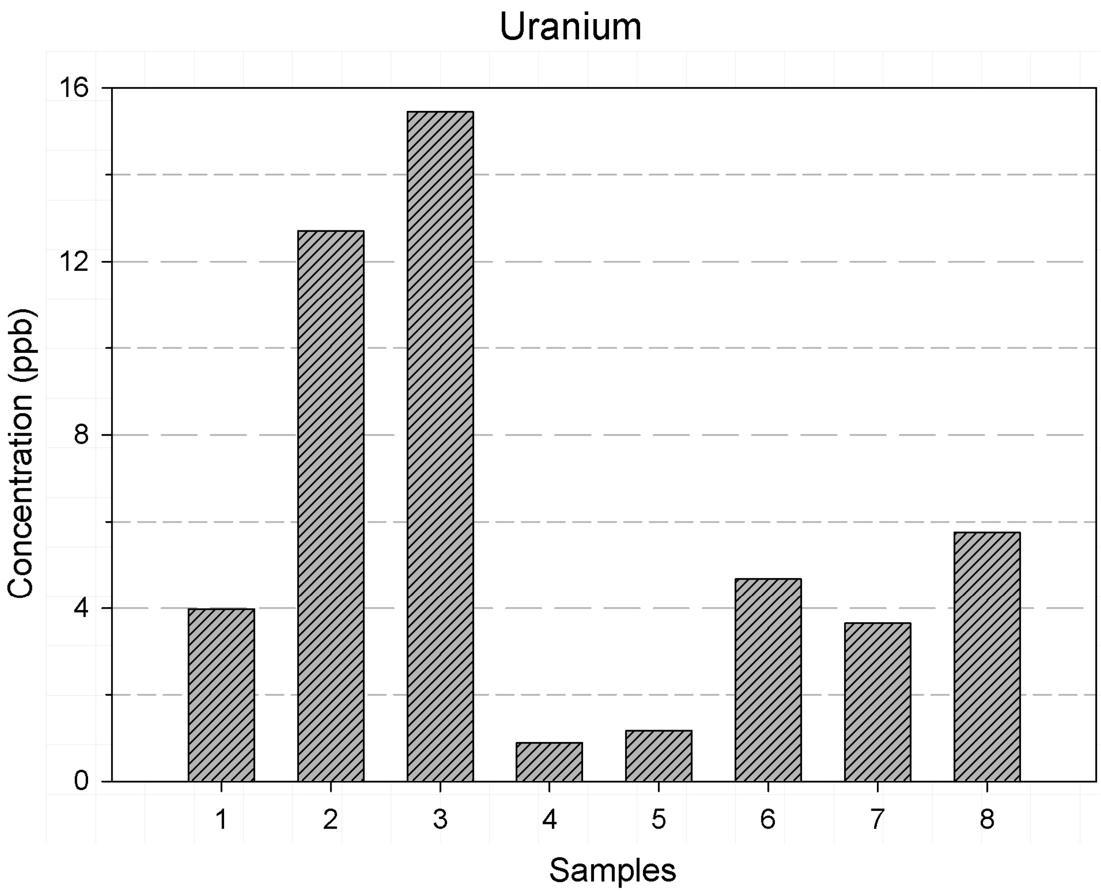

Fig. 4. Uranium levels in cereals.

"Fingerprint" Characterization

Fingerprinting is a technique that uses simple algorithms to predict the location or region of origin (provenance) of the sample under study. Table 2 displays simple ratios of Th/Bi, Th/U and U/Bi. It is clear from the table that certain ratios are distinct and could feasibly be deployed to characterize the breakfast cereal. For example, for sample#1, the Th/Bi ratio is about 8 and for sample#7 it is 0.65. These ratios could possibly be employed to identify these two cereals, and their country of origin. Likewise sample#1 could be identified by its Th/U ratio, which is 24, the one that stands out among the rest. In the same vein, sample#2 could be characterized by a U/Bi ratio of 1.8. The usefulness of these data cannot be underestimated. In addition, the trend of the data in Table 2 could be used to earmark certain breakfast cereals for remediation by determining which are above the average value. Clearly, samples 1 and 2 stand out and could be considered for some form of remedial treatment, to remove the elevated thorium concentration. Similarly, in the cases of Th/U and U/Bi samples #1 and #2 are appreciably the average values of their respective groups, and here again could be considered for application of remedial measures. Fingerprint characterization therefore, serves two beneficial purposes: (i) to "provenance" the breakfast cereal; and (ii) to determine which ones could undergo remediation.

Table 2. Ratios for fingerprinting studies.

Ratio/Sample	#1	#2	#3	#4	#5	#6	#7	#8	Ave
Th/Bi	8.1	4.8	2.2	2.4	1.9	1.8	0.65	1.3	2.9
Th/U	24	2.7	0.76	7.8	6.9	2.6	2.4	1.1	6.0
U/Bi	0.33	1.8	2.9	0.30	0.27	0.71	0.28	1.2	0.97

Remediation / Impact of the study

No previous research of this nature exists in the documented literature. In view of this, the major impact of the study is that the research is seminal and constitutes a baseline study in sustainable development. By remediation it is meant that the environment related to the production of the breakfast cereal could undergo some form of restorative treatment to minimize pollution by the elements under study. As mentioned earlier specific agricultural conditions could evoke contamination in plant-derived foodstuffs. Contaminated soil conditioners and manure, polluted irrigation water, and undesirable pesticides could be partially responsible for the elevated levels of the trace elements of interest. Of course, the equipment used for processing these cereals could also be contaminated. However, it seems unlikely that elevated levels of Bi, Th or U could be present in the equipment or machinery. Therefore, what remains is the potential contamination of the soil and water from the surrounding area that cultivate the plant-based cereals. Our study therefore, is an exercise in sustainability and suitable remedial measures could be adopted to stem the pollution from these heavy metals. Sustainable living has become a global effort and our study makes a definite contribution to this effort.

CONCLUSION

Our work was directed towards the detection and evaluation of Bi, Th and U in breakfast cereals. The toxicological effects of these trace heavy metals are still under wide clinical investigation, thus it is uncertain to state whether the levels detected here constitute any serious toxicity. However, our research could be considered a benchmarking application to add to the growing body of knowledge related to nutrition and ultimately to sustainable development. We found that it could be feasible to utilize our data for simple fingerprinting exercises to identify certain breakfast cereals. Future work could include speciation of these elements in such cereals.

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