Determination of arsenic content of food and water applied for food processing in Hungary

Theses of PhD dissertation

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1 Introduction

Due to its bizarre and controversial properties, mankind has been concerned about arsenic (As) for ages. Its several chemical forms (in other words, species) have different physiological properties. Concerning its physiological effects, As can occur either in the form of harmless compounds or dangerous poisons; however, its therapeutic and fortifying effects are also well-known. Inorganic As compounds (iAs) are generally more toxic than organic ones. About 90% of As is ingested by human organisms with food and drinking water consumption but it can be absorbed also dermally or by inhalation. Biomethylation of iAs occur in the liver and the resulting metabolites are excreted in the urine. The extent of exposure to As varies with geographical conditions, social and individual habits. Arsenic occurs in surface water mainly in form of several protonated species of arsenite [As(III)] and arsenate [As(V)] ions. Biomethylation of iAs in the environment is mainly achieved by microorganisms. The most relevant biomethylated species are dimethyl arsinic acid, also known as cacodylic acid [DMA(V)] and monomethyl arsonic acid [MMA(V)]. Nevertheless, arsenobetaine (AB) and arsenocholine (AC) may also frequently occur. In Hungary, natural As contamination of food can originate from water used for food processing.

Due to the geological conditions of the Carpathian basin, the aquiferic water of the southeastern region of Hungary is affected by natural As contamination. Several theories on the high As concentration of aquiferic water in Hungary have been postulated, such as streaming of the As-containing thermal water erupting from the depths as well as adsorption/desorption equilibria on the surface of iron oxyhydroxides. One third of the drinking water wells in the aforementioned regions supplies water with an As concentration exceeding the 10 µg/L health limit value set by the 83/1998 EC directive for drinking water in force since 25 December 2003. With the accession to the EU, Hungary received a derogation on the As content of drinking water until 25 December 2009. However, there are still
settlements with inadequate As containing drinking water after the expiration of the derogation date. Since 1 January 2013, supply of the population with bottled drinking water is ensured by the Hungarian Armed Forces in the aforementioned regions, especially in Békés and Csongrád counties.

Thus, first of all, my research topic focused on the investigation of the relationship between As content of food and drinking water. On the other hand, my research work was extended also to the investigation of iAs species [As(III), As(V)] in drinking water, since As toxicity is considerably influenced by the occurrence of its species.

2 Objectives

2.1 Determination of As content of local food and water used for its processing

As coworker of the Hungarian Central Agricultural Office (MGSZHK), as predecessor-in-title of National Food Chain Safety Office, one of my main objectives was to assess the relationship between the As content of food and water used for its processing by applying controlled sampling of the aforementioned items especially in the Hungarian regions affected by natural As contamination. Thus, the sampling campaign organized by Hungarian Food Safety Authority was focused on small and medium sized enterprises (SMEs) involved in food processing and catering. Another objective was to estimate the dietary As daily exposure of the population living in the affected regions by grouping the investigated food to correspond to typical Hungarian meals.
2.2 Determination of total As, As(III) and As(V) concentration in public well water

Joining the Environmental Chemistry and Bioanalytical Laboratory at the Institute of Chemistry of Eötvös Loránd University as a PhD student, I was involved in the determination of the total As content of water taken from public wells as well as the As(V) and As(III) concentration ratios by applying a simple, on-site sampling strategy impeding the interconversion of As species. Special attention was paid to obtain reliable results for water sampled from wells in everyday use by an in situ As species separation procedure and to investigate whether this water is suitable for human consumption, irrigation or other household activities.

Starting from the geochemical theory according to which occurrence of oxyanion-forming elements in aquiferic water is an indicator of the presence of specific iAs species, correlation was aimed between the concentration of some oxyanion-forming elements (Mo, U, V and W) as well as As(V) concentration in drinking water taking into account chlorination (max. 0.5 mg/kg) applied by water works, too.

3 Materials and methods

3.1 Determination of As content of local foodstuff and water used for their processing

Between February and March 2010, samples were taken at different SMEs (n = 43) and food industry and catering related large enterprises (n = 14) in 49 settlements of Hungary with special emphasis on the regions affected by natural As contamination. In total, 67 food (bread, croissant, cold meat, cured pork chop, ham, Vienna sausage, hen’s eggs, malt, pickled vegetables, clear soups, stew, cabbage-tomato cream, milk and dairy products, baby food, compotes),
soft drinks and beer samples originating from 12 counties in Hungary were analyzed.

Food samples and water used for their preparation were collected simultaneously in each sampling place. About 90% of water samples were tap water, while the rest was taken from driven wells. Dishes were taken only from catering companies, four of them providing food service at kindergartens and schools. The survey was organized by Food and Feed Safety Directorate of the MGSZHK. For water sampling, 500 mL of polyethylene (PE) vessels with plastic caps were used. The aforementioned water samples and other ones with low dry matter content such as beer, soda water and soft drinks were preserved by acidification with nitric acid. For elemental analysis, samples were diluted with high purity water 10 times prior to analysis.

Liquid samples with higher dry matter content (milk, dairy products, soups, cabbage–tomato cream, sour cherry compote and baby food) were homogenized by a Hauser HB-970 mixer of 700 W. The dissolution of the samples was achieved by microwave-assisted digestion using nitric acid and hydrogen peroxide. For digestion, a Milestone-Ethos Plus instrument with 10 Teflon vessels were used.

For the analysis of water and water-based digested samples, a Thermo Element X-series inductively coupled plasma quadrupole mass spectrometry (Q-ICP-MS) instrument equipped with a CETAC ASX-510 autosampler was used. External calibration ($r^2 > 0.995$) was performed daily with freshly prepared standards in the concentration range of 1–200 μg/L and having Ge as the internal standard. Calibration solutions were prepared in PTFE volumetric flasks by dilution from a stock solution. For quantitative determination, the interference of $^{40}$Ar$^{35}$Cl$^+$ on the signals of $^{75}$As$^+$ was taken into consideration by applying mathematical correction with the aid of the PlasmaLab software provided by the instrument manufacturer.
Solid foodstuffs (bread and croissant, cold meat, cured pork chop, ham, hen’s eggs, pizza ham, malt, pickled beetroot/cabbage/cucumber and Vienna sausage) were homogenized by a Moulinex Moulinette chopper of 800 W. Mineralization of homogenized subsamples of 0.5–2 g was achieved by wetting with nitric acid and magnesium compounds and, then, by dry ashing performed in an electric oven. After dissolution of the ash samples by hydrochloric acid, determination of As was performed with the aid of a UNICAM SOLAAR-M6 flame atomic absorption spectrometer equipped with a hydride generator.

3.2 Determination of arsenic species and oxyanion-forming elements in drinking water

From September to October 2011, water samples (n = 23) were taken from public wells in everyday use, situated alongside roads or crossroads, in various settlements of three different counties of Hungary (Bács-Kiskun, Békés, Csongrád) as well as in the resort area of the capital city (Pest county) in order to determine their As(V) and As(III) concentration ratio. The disinfected water of wells is delivered by state or private water works. In order to prevent the interconversion of As species, cartridges filled with DOWEX® 1-X8 anion exchange material, capable of the on site retention of As(V), were used. Cartridges containing approximately 0.6 g of resin were conditioned by hydrochloric and solution and deionized water. The resulting As(III) containing effluents were preserved with nitric acid. For each water sample, a set of three cartridges was used. Elution of As(V) was achieved by

The concentration of the separated As species was determined by inductively coupled sector field mass spectrometric (ICP-SF-MS) analysis in high resolution (R = 10000) mode. Determination of the concentration of some oxyanion-forming elements (Mo, Se, U, V and W) supplying geochemical information on the samples was also achieved by ICP-SF-MS by applying
medium resolution \((R = 4000)\) and peak jumping. In both cases, indium was used as the internal standard. Validation of the results was achieved by analysis of a NIST 1640 certified reference water standard. The recovery rate obtained for total As concentration was 98 \%, while for Mo, Se and V, this ranged between 97 \% and 104 \%.

Efficiency of As species separation was tested in the laboratory with standard solutions having a concentration of 50 μg As/L. Recovery rate As(III) and As(V) was 99 \% and 90 \%, respectively.

4 New scientific results

1. By determining the arsenic (As) content of 67 food samples (including beverages) and water used for food processing taken from 57 food industrial and catering enterprises by hydride generation atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS), linear correlation could be established between the As concentrations of samples (i.e., soups, vegetable creams, compotes and soft drinks) with high water content and water used for their processing. Similar correlation for food items with higher dry matter content could not be observed.

2. Estimated As intake of the daily lower limit of WHO on the benchmark dose for a 0.5 \% increased incidence of lung cancer \((BMDL_{0.5})\) for As was exceeded in two settlements based solely on the drinking water intake of the population, while in other three with the combined consumption of water and food. The maximum daily As intake achieved only from drinking water might be 3.5 μg/kg bw, while the estimated maximum As intake from a combined water and food ingestion could amount to 3.8 μg/kg bw. Among these five settlements having an As intake exceeding the \(BMDL_{0.5}\), three are located in Csongrád county and the distance between them is less than 55 km.

3. Total As concentration of water originating from public wells of 23 Hungarian settlements obtaining water from aquifers naturally contaminated with
As, and determined by sector field ICP-MS, varied between 7 and 210 μg/L. Total As concentration exceeded the health limit value of 10 μg/L set by the 83/1998 EC directive in the case of 22 settlements. The As concentration of water taken from 43 small and medium-sized as well as 14 large enterprises exceeded the 10 μg/L health limit value in 74% of the samples. Moreover, there was no considerable difference in the As content of water originating from drilled well or tap water.

4. The As(V) and As(III) concentration of drinking water taken from public wells ranged between 5.5 – 163 μg/L and < 0.1 – 44.5 μg/L, respectively. In two thirds of the samples, the As(V) and As(III) concentration ratio was higher than 1.5 and for slightly more than 40% of the samples, this ratio was higher than 7.3.

5. The concentration of some oxyanion-forming elements (Mo, Se, U, V and W) providing information on the redox character of the geochemical environment of aquiferic water was only partially suitable or not at all for the estimation of the occurrence of As species in drinking water. However, their determination supported in a more reliable way the results obtained for the distribution of As species than other on site determined parameter characteristic for water such as pH, conductivity and redox potential.

5 Conclusions, summary

As part of a national survey conducted by MGSZHK in 2010, as predecessor-in-title of NÉBIH, analysis aiming at the determination of As in 67 food samples including beverages was ordered. Water used for food processing was simultaneously sampled. Among the monitored companies, 75% was small and medium-sized enterprises (SMEs). Moreover, 40% of the SMEs were micro entities. The As content of solid foodstuff was determined by hydride generation atomic absorption spectrometry after dry ashing. Foodstuff with high water content and water samples were analyzed by Q-ICP-MS. The As concentration exceeded the 10 μg/L health limit value established by the 83/1998 EC directive.
for drinking water in 74% of the water samples taken from SMEs. The As concentration of food samples with high water content and water used for their production correlated linearly.

The estimated As intake from combined exposure to drinking water and food of the population was on average 40% of the daily benchmark dose limit value of 3 μg/kg body weight/day recommended by WHO that increases the incidence of lung cancer by 0.5% (BMDL\textsubscript{0.5}) for As. Five settlements had higher As intake than the BMDL\textsubscript{0.5}. Three of these settlements are located in Csongrâd county and the distance between them is less than 55 km. The maximum As intake might be 3.8 μg/kg body weight/day.

Twenty-three water samples were collected from public wells from three different counties as well as the resort area close to the capital city, having historically high natural As occurrence in Hungary, for speciation analysis of As(V) and As(III). In order to prevent interconversion of As species in the samples, a simple field separation method was applied by using SPE cartridges filled with an anion exchange material prior to the analysis by ICP-SF-MS. Total As concentration level in the samples was confirmed to be higher than the 10 μg/L health limit for drinking water in 22 samples. Thus, the total As concentration of the samples ranged between 7.2 and 210 μg/L. In two thirds of the samples, the As(V) concentration exceeded by factor 1.5 than that of As(III). Arsenic speciation in drinking water is still more reliable than the determination of the concentration of oxyanion-forming elements (i.e., Mo, Se, U, V and W) as indicators of the oxidative character of the geochemical environment and hence, occurrence of As(V) in water.
6 Publications

Publications in the topic of the dissertation

   IF: 2.610

   IF: 3.583

   IF: -

Oral presentations in the topic of the PhD dissertation


Poster presentations in the topic of the PhD dissertation
