Determination of antimony and phthalate esters in mineral water after leaching from polyethylene terephthalate bottles

Theses of PhD dissertation

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1. Introduction

Water is the basis of all life on Earth. Water represents about 70% of the body weight of an adult. This percentage decreases gradually with aging. Water present in the living organisms ensures circulation, regulates blood pressure, enables absorption and transport of food, influences blood composition, thermoregulates elimination of metabolites, maintains cellular osmotic pressure and regulates the temperature of the body. The daily water intake required by the organism of an adult is about 2.5 L. Television and newspaper advertisements as well as water bottle labels alluding to pristine springs and mountain creeks hint that consumption of bottled water protects human health. Therefore, consumption of mineral water has considerably increased in the past decades. To this, aversion of people to water disinfection byproducts also contributes. In the past three decades, mineral water consumption in Hungary increased from 3 L/year to 116 L/year per capita. According to water consumption data for 2012, Hungary occupied the fifth place in the ranking of European countries after Italy, Germany, Belgium and Spain. Polyethylene terephthalate (PET) belonging to the family of polyesters is one of the most popular food packaging materials. It is mostly used for bottling liquids. Compared to glass, PET is not fragile and less toxic elements are leached from it. Antimony (Sb) may be one of these toxic elements, since Sb(III) oxide is added as a catalyst during the polycondensation used for PET production. Antimony and its compounds are classified by US EPA and European Union (EU) as priority contaminants. Thus, the 98/83/EC directive established 5 μg/L health limit value for Sb in drinking water. Contrary to other plastic materials such as PVC, there is no need to add plasticizers such as phthalates showing endocrine activity during PET production. Although leaching of contaminants by contact between food and packaging material is strictly regulated in the EU through regulation 10/2011/EC, presence of Sb and phthalate esters in PET-bottled water has already been reported. Although, some researchers consider unnecessary studying contaminant leaching from PET into water at higher temperature values, PET-bottled mineral water can be exposed to extreme temperature, exceeding even 65 ºC in summer in cars, their closed parking or storage places with poor ventilation. Thus, it is reasonable to expose PET-bottled mineral water to short temperature and artificial illumination stress effects.

2. Objectives

During bibliographic search, I have not found any relevant literature data on investigation of the presence of Sb and/or phthalate esters in PET-bottled Hungarian mineral water. One of the consequences of the ever increasing market of bottled water is the need for modern instrumental analytical techniques for the accurate determination of leaching compounds potentially harmful to human health. Taking into account the sometimes contradictory information published separately on Sb and phthalate ester contents of PET-bottled water, the objectives of this PhD thesis were the execution of the following systematic and integrated investigations:

- Determination of Sb concentration of PET by inductively coupled plasma sector field mass spectrometry (ICP-SF-MS) after development of an adequate microwave-assisted (MW) acid digestion procedure for the polymer material;
- Identification of phthalate esters in PET by pyrolysis gas chromatography mass spectrometry (GC-MS);
- Study of Sb and phthalate concentration change in PET-bottled (non)carbonated mineral water after potential leaching from the packaging material by using ICP-SF-MS and GC-MS after liquid-liquid extraction, respectively;
- Execution of model experiments aiming at improper storage to follow the change in the Sb and phthalate ester concentration of water taking into account:
  (a) study of mineral water commercialized in Hungary;
  (b) study of new and recycled PET bottles;
  (c) bottle volume;
  (d) storage time;
  (e) storage temperature.

Thus, my work aimed not only at obtaining information on the consequences of improper storage of water through determination of Sb and phthalate esters but also on the quality of the PET raw material used for bottle production.

3. Materials and methods

3.1. Sample provenance and labeling

My PhD work started by investigating ten different mineral water brands commercialized in 0.5-L, 1.5-L and 2.0-L PET bottles. Then, systematic investigation was performed on three water brands bottled in PET made either of new or recycled flakes. In the case of these three water brands, their producer also supplied water prior to bottling.

3.2. Determination of Sb content in PET

For the determination of Sb content of PET, I developed an MW-assisted acid digestion method in closed Teflon vessels by using a HPR 1000/10s Ethos (Milestone, Minnesota, USA) equipment. The total organic content of the samples was checked by using an Analytik Jena MULTI N/C 2100 S TOC/TN equipment. The Sb content was determined by an Element2 Thermo Finnigan ICP-SF-MS instrument at low resolution. Quantitative determination of Sb in PET-bottled bottled mineral water also was made by the ICP-SF-MS.

3.3. Investigation of PET bottles by pyrolysis gas chromatography mass spectrometry

Pyrolysis experiments were carried out on a Pyroprobe 2000 pyrolyser (Chemical Data Systems) on-line coupled with a GC–MS (Agilent Techn. Inc. 6890 GC/5973 MSD) instrument. For the pyrolysis GC-MS experiments, samples were cut from the neck of the bottle where contact of PET with water was minimal.

3.4. Determination of phthalate concentration of PET-bottled mineral water

For the quantitative determination of phthalates in mineral water, a Varian 4000 tandem GC–MS system (Varian, Walnut Creek, USA) was used. The apparatus consisting of Varian 3800 GC and Varian 4000 ion trap MS contained also an automatic sampler and a programmable injector (Varian 1079). Phthalate were extracted CH_2Cl_2. Samples were preconcentrated and stored at 4 ºC. Sample derivatization was not applied. In both cases, GC-MS measurements were done in SIM mode at m/z 149.

4. New scientific results

1. The Sb concentration of water samples prior to bottling originating from the mineral water producer was below the 2.3 ng/L detection limit of the ICP-SF-MS analytical technique. The blank values for diisobutyl phthalate (DiBP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and bis(2-ethylhexyl) phthalate (DEHP) having as limit of quantification (LOQ) 3,0 ng/L, 6,6 ng/L, 6,0 ng/L and 16,0 ng/L, respectively, were reproducibly much higher than the corresponding LOQ values.

2. The Sb concentration of the investigated PET materials ranged between 210 and 290 mg/kg, while among the investigated phthalates, DEHP, DiBP and DBP could be determined by pyrolysis GC-MS. According to my calculations, the peak area of DEHP related to the bottles made of recycled PET in 30% and solely from virgin PET flakes ranged between 3.2 and 4.2.

3. The Sb concentration leaching from 0.5-L, 1.5-L and 2.0-L PET bottles of 10 different (non)carbonated Hungarian mineral water brands varied between 0.03 μg/L and 0.8 μg/L. Therefore, the Sb concentration of the investigated water did not exceed the health limit value of 5 μg/L established for drinking water by the EU in the 98/83/EC directive. Moreover, the Sb concentration in carbonated mineral water was about 1.5-fold higher than in the noncarbonated samples having a similar expiry date and stored in an identical way.

4. Phthalates in the similarly stored carbonated mineral water samples could not be detected. The phthalate concentration in mineral water brand ″A″ (whose bottles were solely made of virgin PET flakes) was negligible. The concentration of DiBP, DBP, BBP and DEHP varied as it follows: <3.0 ng/L – 0.2 μg/L, <6.6 ng/L – 0.8 μg/L, <6.0 ng/L – 0.1 μg/L and <16.0 ng/L – 1.7 μg/L, respectively for noncarbonated water samples stored exclusively for 90 days at different temperature (22 °C – 60 °C). The occurrence of DEHP was the highest in the investigated samples. However, its concentration did not exceed the 6 μg/L limit value set for food by US EPA.

5. Due to the increased contact surface area, the Sb content of mineral water stored in 0.5-L PET bottles was higher by 40% and 80% than in the ones stored in 1.5-L and 2.0-L PET bottles, respectively. The DEHP content of water stored in 0.5-L PET bottles was higher by 20% - 50% compared to the samples stored in PET with larger volume. Moreover, linear correlation could be established for the leaching of Sb and DEHP.

6. By investigating the effect of storage time on leaching, the increase in the Sb concentration could be characterized by a saturation curve and the Sb concentration reached 0.7 – 0.8 μg/L. Among the investigated phthalates, leaching of DEHP could be described with a second order polynomial fit. However, leaching of DEHP achieved its maximal value of 1.2 μg/L only after a storage exceeding 1200 days.

7. The increase of the storage temperature also increased the Sb concentration of the samples. Thus, the Sb concentration of water samples thermosthated at 60 ºC for 72 hours and 70ºC for 9 hours reached 2 μg/L. Similarly, storage of water samples at 60 ºC caused a considerable increase in the DEHP concentration. However, after 72 hours, the amounts of this phthalate decreased presumably due to its degradation.

5. Conclusions, summary

During my PhD work, first, I mapped the Sb content of ten (non)carbonated Hungarian PET-bottled mineral water brands as a function of storage time. The Sb concentration of the carbonated samples was higher than those of noncarbonated ones. However, the Sb concentration values of the samples never exceeded the health limit value of 5 μg/L for Sb in drinking water set by 98/83/EC directive. Then, in total, three mineral water brands bottled in PET made of either solely virgin or also recycled polymer were chosen. For these brands, their mineral water companies also supplied water prior to bottling. By performing experiments modelling improper storage conditions, the Sb concentration in water upon short time (max. 72 h), temperature (max. 70 ºC) and artificial illumination stress exposure was determined. The concentration of the most commonly used phthalate esters as plasticizers were also determined in the aforementioned three water brands. In the noncarbonated mineral water, BBP, DBP, DiBP and DEHP were determined in the the ng/L – μg/L concentration range. The guideline value of 6 μg/L in food set by EPA was not achieved even for DEHP present in the samples in the highest concentration. The phthalate esters detected in the noncarbonated water samples could not be detected in the carbonated ones, for which the acid-base catalyzed ester hydrolysis may be responsible. The highest Sb and phthalate ester concentration was determined in the 0.5-L PET bottles having the highest contact surface area related to water volume. The Sb concentration in noncarbonated water samples could be characterized by a saturation curve, while, by extending the temperature stress experiments on phthalate esters, the change in the DEHP concentration as a function of time could be described by a second order polynomial fit. By thermosthating the samples at 60 ºC, the Sb concentration increased and reached the 2 μg/L value. At the same time, a similar and unequivocal trend could not be observed for phthalates perhaps due to the antagonistic leaching and heat and/or photolytic degradation effects. Water stored in PET bottles made solely of virgin flakes had the lowest Sb and phthalate content that can be related to the quality of the polymer used.

Determination of the Sb and phthalate content of mineral water by performing experiments with harmonized parameters means a novel, integrated approach compared to the studies performed so far separately for these emerging inorganic and organic water pollutants in bottled water.

6. Publications

Publications in the topic of the dissertation:

1. Szilvia Keresztes, Victor G. Mihucz, Enikő Tatár, István Virág, Gyula Záray: **Leaching of antimony from polyethylene terephthalate (PET) bottles into mineral water**
Science of the Total Environment 407 (2009) 4731-4735
Impact factor: 2,905

2. Szilvia Keresztes, Enikő Tatár, Zsuzsanna Czégény, Gyula Záray, Victor G. Mihucz: **Study on the leaching of phthalates from polyethylene terephthalate bottles into mineral water**
Science of the Total Environment 458–460 (2013) 451-458
Impact factor: 3,163

Oral presentations in the topic of the PhD dissertation:

1. **PET-palackokban tárolt ásványvizek Sb-tartalmának meghatározása**
Keresztes Szilvia, Mihucz Viktor Gábor, Tatár Enikő, Virág István, Záray Gyula
51. Magyar Spekrokémiai Vándorgyűlés, Nyíregyháza, 2008. június 30. – július 02.

2. **Effect of storage conditions on antimony leaching from PET bottles into mineral water in Hungary**
Szilvia Keresztes, Victor Gábor Mihucz, Enikő Tatár, Gyula Záray
3rd Sino-Hungarian Symposium on „Environmental impact of inorganic and organic pollutants on ecosystems”, Budapest, 03 – 04 September 2009

3. **Az antimon polietilén-tereftalát-palackokból magyarországi ásványvizekbe történő kioldódásának vizsgálata**
Keresztes Szilvia, Mihucz Viktor Gábor, Tatár Enikő, Virág István, Záray Gyula
XV. Nemzetközi Vegyészkonferencia, Marosvásárhely, 2009. november 12 – 15.

4. **PET-palackokból kioldódó antimon és néhány műanyag lágyító mennyiségének meghatározása hazai ásványvizekben**
Keresztes Szilvia, Mihucz Viktor Gábor, Tatár Enikő, Perlné Molnár Ibolya, Záray Gyula
Fiatal analitikusok előadóülése, Budapest, 2010. február 25.

5. **Study of leaching of antimony and phthalates from polyethylene terephthalate bottles into mineral water**

Szilvia Keresztes, Enikő Tatár, Victor G. Mihucz, Ibolya Molnár-Perl, Gyula Záray

Colloquium Spectroscopicum Internationale XXXVII, Rio de Janeiro, 28 August – 02 September 2011

6. **Antimon és ftálsavészterek kioldódása polietilén-tereftalátból ásványvizekbe**

Keresztes Szilvia, Perlné Molnár Ibolya, Tatár Enikő, Záray Gyula, Mihucz Viktor Gábor

55. Magyar Spekrokémiai Vándorgyűlés, Veszprém, 2012. július 09 – 11.

Poster presentations in the topic of the PhD dissertation:

1. **Leaching of Sb from polyethylene terephtalate (PET) bottles into mineral waters and soft drinks**

Szilvia Keresztes, Victor Gábor Mihucz, Enikő Tatár, István Virág, Jun Yao, Gyula Záray

XIII Italian-Hungarian Symposium on Spectrochemistry Environmental Contamination and Food Safety, Bologna, 20 – 24 April 2008

2. **Changes of some phthalate concentration in mineral water as a function of brand and storage**

Szilvia Keresztes, Victor Gábor Mihucz, Enikő Tatár, Ibolya Perl-Molnár, Gyula Záray

XIV Hungarian-Italian Symposium on Spectrochemistry, Sümeg, 2011. október 5 – 7.