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# Migration of antimony from PET bottles into beverages: Determination of the activation energy of diffusion and migration modelling compared to literature data

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**Migration of antimony from PET bottles into beverages:  
Determination of the activation energy of diffusion and  
migration modelling compared to literature data**

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Food Types:	Beverages, Fruit juices, Drinking water

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6 **Migration of antimony from PET bottles into beverages:**  
7 **Determination of the activation energy of diffusion and migration**  
8 **modelling compared to literature data**  
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## Abstract

Plastics bottles made from polyethylene terephthalate (PET) are increasingly used for soft drinks, mineral water, juices and beer. In this study a literature review is presented concerning antimony levels found both in PET materials as well as in foods and food simulants. On the other hand, 67 PET samples from the European bottle market were investigated for their residual antimony concentrations. A mean value of  $224 \pm 32$  mg/kg was found, the median was 220 mg/kg. Diffusion coefficients for antimony in PET bottle materials were experimentally determined at different temperature between 105 °C and 150 °C. From these data the activation energy of diffusion for antimony species from the PET bottle wall into beverages and food simulants was calculated. The obtained value  $189 \text{ kJ mol}^{-1}$  was found to be in good agreement with published data on PET microwave trays ( $184 \text{ kJ mol}^{-1}$ ). Based on these results the migration of antimony into beverages was predicted by mathematical migration modelling for different surface/volume ratios and antimony bottle wall concentrations. The results were compared to literature data as well as international legal limits and guidelines values for drinking water as well as migration limit set from food packaging legislation. It was concluded that antimony levels in beverages due to migration from PET bottles manufactured according to state-of-the-art can never reach nor exceed the European specific migration limit of  $40 \mu\text{g/kg}$ . Maximum migration levels caused by room temperature storage even after 3 years will never be essentially higher than  $2.5 \mu\text{g/kg}$  and will be in any case below the European limit of  $5 \mu\text{g/kg}$  for drinking water. The results of our study confirm that the exposure of the consumer by antimony migration from PET bottles into beverages and even into edible oils reaches approximately 1% of the current TDI established by WHO. Having substantiated such low antimony levels in PET bottled beverages the often addressed question on estrogenic effects caused by antimony from PET bottles appears to be groundless.

**Keywords:-** Plastic bottles, migration, polyethylene terephthalate (PET), antimony, diffusion coefficients, activation energy of diffusion, juices, mineral water

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For Peer Review Only

## Introduction

Plastics bottles made from polyethylene terephthalate (PET) are increasingly used for beverages like soft drinks, mineral water, juices and beer. In 2007 the world-wide consumption of PET was about 15 Mio. tons (Plastics Europe 2008). Most of the PET resin was sold as food grade material for beverage packaging. In comparison to other packaging plastics, PET is one of the most inert polymers with good barrier properties against moisture, oxygen and carbon dioxide and with a very low migration tendency of its constituents. However, migration of substances from PET bottles into beverages is not completely negligible. Polymer additives, catalyst residues, degradation products, polymerisation side-product or residual monomers are potential migrants. Mass transfer of a migrant from PET polymer into food depends on several factors such as storage time and temperature, concentration of the migrant in the polymer, type and nature of the migrant and its solubility in food. Migration kinetics of several organic impurities and additives in PET have been investigated in systematic migration studies within the last years. Target migrants were for instance acetaldehyde (Ewender et al 2003), the PET cyclic trimer (Begley and Hollifield 1990) or UV blocking additives Tinuvin 234 and Tinuvin 1577 (Begley et al 2004).

Recently, we investigated the migration of organic model compounds into food simulants and beverages such as soft drinks, flavoured waters and juices to establish the migration determining mass transfer parameters (Franz and Welle 2008). As suitable model migrants, as more volatile compounds toluene and chlorobenzene and as less volatile substances phenyl cyclohexane, benzophenone and methyl stearate were used. The results of this study showed that food simulants like 50% or 95% ethanol which cause a slight swelling of the PET polymer matrix do increase the migration significantly in comparison to usual beverages. Such high alcoholic simulants can therefore be considered as worse case test media for compliance testing of PET beverage bottles. On the other hand, the aqueous food simulants 3% acetic acid, water and 10% ethanol lead in many cases to an underestimation of migration of organic constituents in comparison to beverages.

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6 One important conclusion of this study was that the migration of organic compounds  
7 from the bottle wall into beverages is largely controlled by the diffusion coefficient in  
8 the polymer. The partition coefficient which represents the ratio between the  
9 concentration of a migrant in the polymer and in the food at the equilibrium plays a  
10 minor role only. Therefore, for the predictive evaluation of compliance of PET bottles  
11 knowledge of the diffusion coefficients of potential migrants is highly important since  
12 it allows to calculate the concentration of a migrant in the foodstuff under certain  
13 storage conditions.  
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21 Not only organic components are able to migrate from the PET bottle into the bottled  
22 beverages but also inorganic substances, for instance residues from polymerisation  
23 catalysts can leach from the polymer. The release of inorganic substances from  
24 beverage bottles made of glass versus PET has been investigated in a few studies  
25 (see literature review below). Very recently, a comprehensive study was published in  
26 which drinking water contamination from bottle materials was investigated for 57  
27 chemical elements (Reimann et al 2010). In this study the only element which was  
28 higher concentrated in PET bottled water was antimony with a 21-fold concentration  
29 over glass. All other elements were either comparable in PET and glass bottled water  
30 or considerably higher in glass bottled water. These parameters were in particular  
31 Cer (19-fold higher in glass), Lead (14-fold), Aluminium (7-fold) and other. The higher  
32 concentrations of antimony in PET bottle water is expected, because antimony  
33 trioxide ( $Sb_2O_3$ ) or its reaction product with ethylene glycol is widely used as  
34 polycondensation catalyst for manufacturing of PET. The antimony catalyst offers a  
35 high catalytic activity and has a low tendency to catalyse side reactions. In addition  
36 antimony does not engender undesirable colours (Duh 2002). In principle the  
37 polymerisation catalyst remains in the PET polymer.  
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52 Within the last decade, several studies on the migration of antimony from PET  
53 bottles into beverages and on exposure levels in mineral water, soft drinks and juices  
54 have been published (see literature review below). In addition antimony, in the form  
55 of the chemical species antimony chloride, has been reported to possess weak  
56 estrogenicity (Choe et al 2003) and since then numerous papers have been  
57 published in which a link between antimony from PET and possible estrogenic  
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6 effects were discussed (see for example Sax 2010). In conclusion, antimony must be  
7 considered as the most important inorganic species which may migrate from the PET  
8 bottle wall into the beverages.  
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11 For prediction of exposure levels, the diffusion coefficients of antimony in PET at  
12 different temperatures are helpful. Haldimann et al (2007) determined the migration  
13 of antimony into ready-to-eat meals under microwave or oven-cooking conditions.  
14 PET trays for ready-to-eat meals consist of crystalline PET. In a second study (Alt et  
15 al 2008) the diffusion coefficients of antimony in PET were determined from 45 °C up  
16 to 150 °C, most probably also crystalline PET trays. In comparison to microwave  
17 trays, PET beverage bottles have typically a significantly lower crystallinity of about  
18 30% to 40%, which might influence the diffusion coefficients of antimony.  
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27 Since measured or predicted values should or need to be compared with established  
28 concentration limits the following is a short review of existing regulatory antimony  
29 levels.. According to the German BfR recommendations the maximum concentration  
30 of antimony in PET bottles should not exceed 350 mg/kg (BfR 2010). Limits or  
31 guideline values for antimony in drinking water are specified in several countries:  
32 5 µg/kg in Europe (EU 2003), 6 µg/kg in the United States and Canada (US EPA  
33 2009, Canada 2008), 15 µg/kg in Japan (Japan 2003) and 20 µg/kg by the World  
34 Health Organisation (WHO 2003). These drinking water limits are often used for the  
35 evaluation of antimony concentrations found in bottled beverages. From a legal point  
36 of view, however, these limits are applicable for drinking water itself before it is  
37 bottled. In PET packed beverages the specific migration limits according to  
38 packaging legislation are applicable. This is in Europe 40 µg/kg (EU 2002) and in  
39 Japan 50 µg/kg (JETRO 2009). The US Food and Drug Administration (FDA) has not  
40 specified a special migration limit for antimony from PET packaging materials.  
41 Existing toxicological data suggest for humans a tolerable daily intake (TDI) for  
42 antimony of 6 µg kg<sup>-1</sup> body weight (WHO 2003) which means that a daily  
43 consumption of 360 µg may be tolerable for an adult person with 60 kg body weight.  
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57 The objective of this study was: To determine experimentally the diffusion  
58 characteristics, i.e. activation energy and diffusion coefficients of antimony in PET  
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6 beverage bottle materials. For this purpose it was also necessary to measure and  
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8 compile the typical concentration range of antimony present in PET beverage bottles  
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10 on the European market. Based on the results, the migration of antimony into  
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12 beverages should be predicted by mathematical modelling for different  
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14 surface/volume ratios and antimony bottle wall concentrations. Finally these results  
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16 should be compared with data obtained from a comprehensive literature review on  
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18 antimony diffusion in and migration from PET materials in contact with packaged  
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20 beverages.

## 21 Literature review

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24 Numerous studies have been published either on the antimony content of PET bottle  
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26 material or on antimony concentrations in beverages like mineral water, soft drinks  
27  
28 and juices. According to Duh (2002), antimony concentrations in PET plastics range  
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30 between 190 mg/kg to 300 mg/kg. In the literature, some other studies can be found  
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32 which confirm this concentration range where antimony has been used as catalyst.  
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34 The experimentally determined antimony concentrations found in PET bottles from  
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36 literature data are summarized in Table 1. Much more papers have been published  
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38 on investigations to which extend antimony might migrate from the bottle wall into the  
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40 beverage. A compilation of these literature data for antimony concentrations found in  
41  
42 packaged beverages and in food simulants as a result of a migration test is given in  
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44 Table 2.

45 Place around here Table 1

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47 Place around here Table 2

## 50 Materials and methods

### 51 *PET bottle and pre-form samples*

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56 Altogether 67 PET bottle and pre-form samples were collected from European pre-  
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58 form and PET bottle manufacturers, each with different raw materials, additives or  
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6 recycle source. The samples were supplied directly after manufacture. Information  
7 about the virgin material supplier, the recycle manufacturer and the recycle  
8 content as well as the use of oxygen or acetaldehyde scavengers was provided by  
9 the bottle or pre-form manufacturers in all cases.  
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#### 13 14 15 *Determination of antimony concentration in PET materials*

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18 200 mg of the PET bottle wall or pre-form material was treated with 8 ml conc. nitric  
19 acid for 15 min at 200 °C in a microwave-assisted digestion (similar to EN 13656).  
20 Subsequently the concentration of antimony was determined quantitatively by ICP-  
21 MS according to DIN EN ISO 17294-2 (DIN 2003). Calibration was achieved by  
22 external calibration with antimony standards. As internal control standards rhodium  
23 and rhenium were used. The limit of detection was determined to 1 mg/kg in the PET  
24 material. The antimony concentrations of two bottles were verified by two other  
25 testing laboratories.  
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#### 33 34 35 *Determination of antimony migration kinetics into 3% acetic acid*

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37 To determine the specific migration of antimony into 3% acetic acid, a commercially  
38 available 1.5 l PET softdrink bottle was used. The bottle was supplied from the bottle  
39 manufacturer directly after blowing. The antimony bottle wall concentration was  
40 determined to 260 mg/kg by ICP-MS. The thickness of the bottle wall was  
41 determined to 0.27 mm. The crystallinity of the investigated bottle was determined by  
42 differential scanning calorimetry (DSC) to 43%. The bottle was cut into 5.0x5.0 cm  
43 pieces. The 5.0x5.0 cm pieces are further cut into 1.0x5.0 cm stripes. Five stripes of  
44 1.0x5.0 cm were placed into a steel cell. Glass pellets of 3 mm diameter were added  
45 in order to reduce the dead volume of the extraction cell. The PET material was  
46 extracted with a Büchi Speed Extractor E-916 at 30 °C up to 150 °C. The extraction  
47 cells were filled with 3% acetic acid at a pressure of 100 bar in the extraction cell.  
48 After an extraction time of 1 h, the extraction cell was purged into a glass vial.  
49 Subsequently the extraction cell was filled and extracted again with 3% acetic acid.  
50 The procedure was repeated every hour up to total extraction time of 4 h. For  
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6 another part of the samples the extraction intervals were 1 h, 2 h and 3 h instead of  
7 1 h intervals (total extraction time 6 h). Due to the fact, that the extraction volume  
8 after the Büchi Speed Extractor was not exactly the same, all migration solutions  
9 were filled to exactly 40.0 ml in a volumetric flask before analysing. Quantitative  
10 determination of the antimony concentration in the 3% acetic acid migration solutions  
11 was achieved by ICP-MS according to DIN EN ISO 17294-2 (DIN 2003). Calibration  
12 was achieved by external calibration with antimony standards. As internal standards  
13 rhodium and rhenium were used. The detection limit of the applied method was  
14 2 µg/kg of antimony in 3% acetic acid solution.  
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#### 24 *Determination of diffusion coefficients*

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27 The antimony concentrations of the individual solutions at certain time were plotted  
28 against the square root of time. From the linear correlation of the diffusion coefficient  
29 was determined according to Equation 1. Due to the total immersion of the PET  
30 stripes, the surface area was doubled for the calculation of the diffusion coefficients.  
31 Together with the edge surface and active surface of the PET samples of 51.62 cm<sup>2</sup>  
32 was calculated.  
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38 Place around here Equation 1  
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#### 42 *Migration modelling*

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45 In addition to the experimental migration tests, a migration model based on diffusion  
46 coefficient estimation of chemical substances in polymers has been used (Piringer  
47 2000). This model has been validated within the EU project SMT-CT98-7513  
48 (Piringer 2001, Begley 2005). The calculation of the migration was performed using  
49 the AKTS SML software version 4.51 (AKTS AG Siders, Switzerland).  
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## Results

### *Antimony concentrations on the European PET bottle market*

PET bottles and pre-forms manufactured from materials of 15 different PET raw material suppliers were investigated within this study regarding their antimony concentration in the PET material. All investigated bottles are intended for the use as soft drink or mineral water bottles in Europe. The investigated samples can be considered as a comprehensive overview over the PET bottles available in Europe. The bottles were supplied from pre-form and/or bottle manufactures. In addition to the pre-forms and bottles manufactured from virgin PET materials, pre-forms and bottles with post-consumer PET re-cyclates from eleven different PET recyclers were investigated. In these cases a worst-case situation was evaluated, because pre-forms and bottles made from 100% re-cyclates were investigated in most cases. The 100% approach was used, because the amount of PET re-cyclates in European softdrink and mineral water bottles varies typically between 10% and about 50% and not in every case, the amount of re-cyclates is known by the filling company. PET bottles and pre-forms manufactured from 100% re-cyclates gave in addition more similar results in comparison to bottles manufactured from virgin PET. The results of the experimentally determined antimony concentrations in the PET bottles and pre-forms are compiled in Figure 1. As a result, the mean value from all samples was  $224 \pm 32$  mg/kg ( $n = 67$ ). The median was 220 mg/kg. The bottle wall concentrations determined in this study can be assumed as a basis for the migration calculations (see below).

Place around here Figure 1

### *Determination of the diffusion coefficients of antimony in PET*

The diffusion coefficients of antimony in PET were determined with specific migration kinetics into 3% acetic acid as food simulant. In order to establish the diffusion coefficient at temperatures above the boiling point of water (or 3% acetic acid), a

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6 high pressure migration test was chosen. For that purpose PET bottle wall stripes  
7 (surface area of 51.62 cm<sup>2</sup>) were introduced into a steel extraction cell. The PET was  
8 total immersed with 3% acetic acid at a pressure of 100 bar. The samples were  
9 extracted for 1 h at temperatures from 30 °C up to 150 °C. After the first migration  
10 phase, the migration cells were emptied and filled again with 3% acetic acid. A  
11 second migration phase follows which was either 1 h or 2 h. After the second  
12 migration phase, the migrations cells were emptied again. The procedure was  
13 repeated up to 4 h or either 6 h. All migrations solutions were analysed by ICP-MS  
14 for the antimony concentrations. The antimony concentration in the bottle wall ( $C_{P,0}$ )  
15 was determined by ICP-MS to 260 mg/kg. The results of the migration kinetics are  
16 given in Table 3 and Figure 3. As a result of the migration studies Fickian behaviour  
17 of the antimony migration from the PET bottle wall into 3% acetic acid was found in  
18 all cases. Fickian migration behaviour means that the square root of time versus the  
19 migration follows a linear correlation. From the slope of these linear correlations, the  
20 diffusion coefficients could be calculated according to Equation 1. The  
21 experimentally determined diffusion coefficients are summarized in Table 3. Below a  
22 temperature of 90 °C, the diffusion coefficients could not be determined because the  
23 antimony concentrations in the migration solutions were below of the analytical  
24 detection limit (2 µg/kg) of the applied ICP-MS method. Therefore the determination  
25 of the diffusion coefficients was not possible. The diffusion coefficients of antimony in  
26 PET were also determined by Alt et al (2008) between 45 °C and 150 °C (Table 3  
27 and Figure 3).

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48 From the diffusion coefficients for temperatures between 105 °C and 150 °C the  
49 activation energy of the diffusion were calculated according to the Arrhenius  
50 approach (Equation 2). As a result, the inverse temperature (in K) and the logarithm  
51 of the diffusion coefficient result in a linear correlation (Figure 4). From the slope of  
52 this correlation the activation energy of diffusion of antimony from the PET bottle wall  
53 into 3% acetic acid was calculated to 189 kJ mol<sup>-1</sup>. Alt et al (2008) has determined  
54 activation energy of diffusion of antimony in PET trays of 184 kJ mol<sup>-1</sup> which is in  
55 good agreement with the activation energy found in this study. Due to the fact, that  
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6 the slopes of the logarithm of the diffusion coefficients versus the inverse  
7 temperature are similar in both studies, the activation energies of diffusion are very  
8 similar within both studies. However, the pre-exponential factor  $D_0$  determined in our  
9 study ( $7.5 \cdot 10^{12}$ ) is different from that found by Alt et al ( $1.0 \cdot 10^{14}$ ).  $D_0$  is mainly  
10 influenced by the surface area and the concentration of the migrant in the PET bottle  
11 wall ( $c_{p,0}$ ). Whereas the surface area can be determined very easily, the  
12 concentration of the migrant in the PET bottle wall for inorganic compounds is not  
13 known exactly. According to Duh (2002), Biros et al (2002) and El-Toufaili et al  
14 (2006) the antimony compound present in PET polymer as antimony glycolate  
15 complexes (examples are given in Figure 2). Due to the fact, that antimony is  
16 determined in the PET bottle wall after digestion, the total amount of antimony is  
17 determined. Antimony might be also bound in the PET polymer chain. Polymer  
18 bound antimony, however, will not migrate into beverages. In addition, antimony  
19 trioxide itself will most probably also contribute a negligible part to the antimony  
20 migration. Therefore, the pre-exponential factor determined by Alt et al (2006) is  
21 different compared to the  $D_0$  determined in this study due to most probably a  
22 different amount of migration relevant antimony species in the PET materials used  
23 for the migration studies.  
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#### 42 *Modelling of antimony migration*

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44 The activation energy of diffusion can be used for the calculation of the migration of  
45 antimony from the bottle wall into the beverages. The applied migration model is  
46 based on the Equations 3 and 4 (Crank 1975, Piringer 2000). The term ( $m_{F,t}/A$ ) is the  
47 surface related migration. The concentration of antimony in the PET material is  $c_{p,0}$ ,  
48 the wall thickness is  $d_p$  and the density of the polymer is  $\rho_p$ . The packaging geometry  
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6 (volume foodstuff  $V_F$  and volume polymer  $V_P$ ) as well as the partition coefficient  $K_{P,F}$   
7 is part of the  $\alpha$  factor (Equation 4). The kinetic part is represented by the  
8 temperature-dependent diffusion coefficient  $D_p$ . The term  $q_n$  is a correction factor for  
9 the positive square roots of the equation  $\tan q_n = -\alpha q_n$ . In conclusion, from the  
10 activation energy the diffusion coefficients for antimony in PET can be calculated at  
11 any temperature which can be used for the prediction of the antimony migration  
12 according to Equation 3.  
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24 The experimentally determined activation energy of antimony in PET was used for  
25 the prediction of the migration of antimony into contact media. Figure 5 shows the  
26 results for the calculation of the migration into beverages from the diffusion  
27 coefficients at room temperature (23 °C, 30 °C and 40 °C) up to a storage time of  
28 900 d. Due to the fact, that in our study, the activation energy was only determined  
29 above the glass transition temperature ( $T_g$ ), we assumed the activation energy at  
30 temperatures below  $T_g$  do not change. The data of Alt et al slightly indicate a  
31 different slope of the Arrhenius plot below  $T_g$ , but based on this data a clear  
32 conclusion is not possible, because the data fit also in one linear regression over the  
33 whole temperature range. As a bottle wall concentration of antimony 224 mg/kg as  
34 well as 350 mg/kg was assumed. 224 mg/kg represents the mean value of the  
35 antimony bottle wall concentration found in this study. 350 mg/kg of antimony in the  
36 PET bottle wall is the worst case of the antimony concentration (BfR 2010). It should  
37 be noted here, that due to migration theory (Equation 3) the concentration of  
38 antimony is directly proportional to the migration at certain contact conditions. E.g. if  
39 the antimony concentration in the bottle wall is e.g. by a factor of two lower than  
40 350 mg/kg, the migration at a certain contact time is reduced by the same factor.  
41 According to the discussion above, the applied concentration of antimony in the PET  
42 bottle can be considered as worse case, because parts of the antimony in the PET is  
43 polymer bound and has therefore no contribution to the migration of antimony into  
44 the beverages. The partition coefficient was assumed to  $K = 1$ , which represents  
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6 good solubility of the migrant in the beverage.  $K = 1$  can be therefore considered as  
7 the worst case of the antimony migration into beverages.  
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## 12 Discussion and conclusions 13

### 14 *Prediction of the antimony migration from PET bottles* 15

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18 The most important parameters for the prediction of the migration of a chemical  
19 compound are the concentration of the migrant in the packaging material ( $c_{p,0}$ ), the  
20 diffusion coefficient ( $D$ ) of the chemical species in the polymer as well as the partition  
21 coefficient ( $K$ ) between the polymer and the contact media (Equation 3). The  
22 partition coefficient, however, plays in the case of PET a minor role because the  
23 equilibrium is not reached assuming typical a shelf life of beverages. This is due to  
24 the low diffusivity of the PET polymer (Franz and Welle 2008), which means that for  
25 the prediction of the antimony migration the diffusion coefficients are the most  
26 important factors.  
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30 The diffusion coefficients were determined for temperatures between 105 °C and  
31 150 °C. The results of this study indicate that the migration of antimony follows a  
32 Fickian behaviour. From the temperature dependence of the diffusion coefficients,  
33 the activation energy of diffusion of antimony in the PET bottle was determined to be  
34 189 kJ mol<sup>-1</sup>. This is in good agreement with literature data for the antimony  
35 migration of 184 kJ mol<sup>-1</sup> in a PET microwave tray. The activation energies were  
36 subsequently used for the calculation of the migration of antimony from the PET  
37 bottle wall into beverages under different conditions (Figure 5). With respect to food  
38 safety and consumer protection, the lower and therefore more conservative  
39 activation energy of 184 kJ mol<sup>-1</sup> was used for the prediction of the antimony  
40 migration. In a first scenario, a bottle wall concentration of 224 mg/kg was assumed.  
41 From this a maximum concentration of about 0.9 µg/kg can be calculated after a  
42 storage time of 300 d at 23 °C ( $c_{p,0} = 224$  mg/kg) for a 500 ml PET bottle. In a  
43 second scenario, migration was calculated for a bottle wall concentration of  
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6 350 mg/kg, which is the maximum concentration of antimony specified according to  
7 the German BfR recommendations (BfR 2010).  
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10 As a result, the antimony migration even under worst case considerations is far  
11 below the specific migration limits of antimony of 40 µg/kg given by European  
12 packaging legislation. Under realistic storage conditions, this migration limit can  
13 never be reached. The migration values are calculated for two different bottle  
14 volumes (500 ml and 1500 ml). Larger PET bottles will lead to a lower antimony  
15 migration due to the more favourable surface/volume ratio, which result in a factor  
16 1.43 higher antimony concentration in a 500 ml PET bottle in comparison to a  
17 1500 ml bottle under otherwise equal contact conditions. Under realistic room  
18 temperature storage conditions (e.g. 23 °C), the lowest drinking water limit (5 µg/kg)  
19 can also not be exceeded (calculated for storage times up to about 900 d).  
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28 The literature data compilation in Table 2 gives an overview of the antimony  
29 migration studies from PET bottles beverages published over the last 10 to 15 years.  
30 The data show that the antimony concentrations did not significantly change over the  
31 last decade. From the literature data given in Table 2 it is hard to derive, how many  
32 different mineral water, softdrink and juices samples were investigated within the last  
33 10 to 15 years. But the amount is definitively several hundreds of beverage bottles.  
34 The samples are coming from many different countries all over the world. However,  
35 not in every case it is clear if PET bottles were investigated. On the other hand, most  
36 of the literature studies were published from 2000 to 2010. It is therefore most likely  
37 that the majority of the investigated mineral water and soft drinks are packaged in  
38 PET. Most of the samples were drawn from local markets and the filling date as well  
39 as the storage conditions are not or only roughly known. In addition, the bottle wall  
40 concentration of antimony was not determined in most cases, which makes a  
41 comparison of the results of different migration studies difficult. However, most  
42 probably the bottle wall concentrations are in a similar range as found in this study  
43 and as given in Figure 1 or Table 1. The storage time before analysing is most  
44 probably only a few months. Assuming a storage time of only a few months at room  
45 temperature before analysing, the antimony concentrations found in the literature are  
46 in good agreement with the calculated data from this study, where a storage of a  
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6 beverage at 23°C up to one year would lead to a migration below of about 1 µg/kg.  
7 The calculated migration in this study (Figure 5) is also in good agreement with  
8 published data (e.g. Figure 2 in Keresztes et al 2009). Keresztes et al found that an  
9 antimony concentration of about 1 µg/kg in a 1.5 l PET bottle after storage of 950 d  
10 at room temperature.  
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15 In a very recent study, Hansen et al (2010) found antimony concentrations up to  
16 about 14 µg/kg in red juices. The authors investigated ready to drink juices or  
17 cordials, which should be diluted with water prior to consumption. It is interesting to  
18 note, that the highest concentrations (4 µg/kg to 8 µg/kg) found by Hansen et al are  
19 coming from one specific brand packed in completely different packaging materials  
20 e.g. PET, cardboard and glass. In addition, the highest concentration was found in  
21 the glass packed juice. Therefore, the antimony concentrations found by Hansen et  
22 al (2010) cannot be related to the packaging material but to the juice itself,. This  
23 conclusion which was also taken into consideration by Hansen et al, was supported  
24 by the fact, that the concentrations of antimony in cordials (before dilution) were  
25 significantly higher than the ready to drink juices. Cordials have to be concentrated  
26 which increases also the amount of inorganic compounds in the juice. In conclusion,  
27 the antimony contamination found by Hansen et al (2010) occurs in the juices before  
28 filling and is due to another contamination way. The migration of antimony from the  
29 PET bottle wall plays here a minor role.  
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#### 44 *Consumer safety considerations*

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46 It is very noteworthy that, as a result of the literature study, no single antimony  
47 concentration of the reported beverage samples bottled in PET exceeded the lowest  
48 drinking water concentration limit of 5 µg/kg. Furthermore, all mean or median values  
49 are found below 1 µg/kg. The specific migration limit for antimony of 40 µg/kg for  
50 bottled water set by food packaging legislation in Europe is far above any of the  
51 reported beverage samples covered by our literature search.  
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59 According to the extremely low diffusion coefficients of antimony species in PET at  
60 room temperature and somewhat elevated temperature up to 40°C, the resulting

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6 migration is extremely low (compare Figure 5). For example, the 5 µg/kg drinking  
7 water limit will be reached after about 10 years storage of a PET packed beverage  
8 (500 ml,  $c_{p,0} = 350$  mg/kg, worst case scenario). It is interesting to note, that the  
9 equilibrium after such a long room temperature storage is still not established. At  
10 40 °C the 40 µg/kg packaging threshold limit is reached under the above mentioned  
11 worst case conditions after about 12 years. At 80 °C the storage time for establishing  
12 a migration of 40 µg/kg is significantly reduced to about 33 h, however, still far above  
13 typical hot fill conditions of about a only few minutes at 80 °C. The results of our  
14 study substantiate as a matter of fact that the European specific migration limit of  
15 40 µg/kg can never be exceeded in PET bottled beverages even when they were  
16 stored over years under worst conditions of e.g. 40 °C and even at higher  
17 technological relevant antimony levels in PET. This conclusion leads immediately to  
18 another consequence: antimony compliance testing on PET bottles for beverages  
19 and fatty liquids including edible oils is superfluous. This conclusion is  
20 complementary to one of our previous studies (Störmer et al 2004) on the migration  
21 behaviour of PET with regard to PET monomers and concerning overall migration. In  
22 this study we concluded that compliance testing on PET with regard to PET  
23 monomers and overall migration is unnecessary because the specified migration  
24 limits can never be exceeded by PET materials which are today on the market.  
25 Migration modelling considerations can replace here migration testing.  
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42 WHO (WHO 2003) has set a tolerable daily intake (TDI) value for antimony of 6 µg  
43 antimony per kg body weight. This would translate into 360 µg intake for an adult  
44 with 60 kg body weight. The Swiss BAG (BAG 2005) came to the conclusion that the  
45 concentrations of antimony found in bottled mineral water samples can be  
46 considered as safe, because a consumption of 3 l of a mineral water per day with  
47 1.2 µg/kg antimony which was the highest value found in the BAG study will result in  
48 only 1% of the TDI. Therefore the migrated amounts of antimony relative to the  
49 accepted tolerable daily intake (TDI) show that exposure is currently not of  
50 toxicological concern (BAG 2005). The results of our study are not only fully  
51 supportive to this conclusion which is based on analytical survey data but allow  
52 furthermore the prospective conclusion that as long as PET materials are  
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6 manufactured with current levels of antimony, exposure from PET bottles through  
7 beverages and edible oils would be less than 1% of the current TDI. Finally, having  
8 substantiated such low antimony levels in PET bottled beverages the above  
9 addressed question on estrogenic effects caused by PET bottles appears to be  
10 groundless.  
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Table 1: Literature data for antimony concentrations determined in PET bottles

Determined antimony concentrations	Reference
160 ppm and 230 ppm (n = 2)	Fordham et al 1995
168 ppm to 216 ppm (n = 6) 58 ppm (n = 1) <sup>[a]</sup> <2 ppm (n = 2)	Nishioka et al 2002
188 ppm to 268 ppm (pellets, n =6) <2 ppm <sup>[b]</sup> (pellets, n = 4) 189 ppm to 264 ppm (bottles, 11) <2 ppm (bottles, n = 7) <sup>[c]</sup>	Ohkado et al 2005
154 ppm to 275 ppm (n = 5) <sup>[d]</sup>	Takahashi et al 2008
213 ±35 ppm (n= 9)	Westerhoff et al 2008
210 ppm to 290 ppm (n = 10)	Keresztes et al 2009

<sup>[a]</sup>recycled PET, <sup>[b]</sup>virgin PET pellets with germanium as catalyst (41 ppm to 80 ppm), <sup>[c]</sup>virgin PET bottles with germanium catalysts (49 ppm to 82 ppm), <sup>[d]</sup>additional data from Chinese (n = 72) and Japanese (n = 105) market are given in Figure 1 of Takahashi et al 2008

Table 2: Literature data for antimony concentrations determined in bottled beverages and food simulants

Investigated samples	Determined antimony concentrations	Remarks	Reference
PET pellets	Individual conc. 3% acetic acid (10 d at 40 °C): 2.7 ppb and 1.2 ppb, 3% acetic acid (2 h at 100 °C): 3.9 ppb and 2.6 ppb, 15% ethanol (10 d at 40 °C): 2.3 ppb and 1.1 ppb, olive oil <0.01 ppb (both conditions)	3 g of PET pellets were totally immersed with 20 ml of food simulant.	Fordham et al 1995
56 European bottled mineral water brands	Individual conc. 0.003 ppb to 1.06 ppb; median conc. 0.17 ppb	Packing materials were not specified	Misund et al 1999
One orange juice sample	Conc. 2.2 ppb	Packing material was not specified	Ulrich 2000
42 Mineral water brands from Canada (199 different samples)	Mineral water: average conc. 0.32 ppb (n = 42), spring water: average conc. 0.30 ppb (n = 102), distilled water: average conc. 0.17 ppb (n = 25), soda water: average conc. 0.29 ppb (n = 19), tap water: average conc. 0.17 ppb (n = 11), individual conc. 0.03 ppb to 1.31 ppb	Packing materials were not specified. Samples drawn December 1995 to February 1996	Dabeka et al 2002
Food simulants 3% acetic acid and 95% ethanol	Individual conc. in 3% acetic acid: 0.15 µg dm <sup>2</sup> to 0.57 µg dm <sup>2</sup> (n = 7, assuming a 1 l bottle with 6 dm <sup>2</sup> surface area will result in concentrations between 0.90 ppb to 3.42 ppb), in 95% ethanol: <0.3 µg dm <sup>2</sup>	Storage for 10 d at 40 °C, surface volume ratio of 2 dm <sup>2</sup> for 100 ml simulant	Störmer et al 2004
Mineral water	Average conc. (PET): 0.43 ppb (n = 49); average conc. (glass): factor 3.5 lower	Samples were packed in glass and PET.	BAG 2005

Investigated samples	Determined antimony concentrations	Remarks	Reference
	than PET (n = 20)		
48 Bottled waters from the Swedish market	Individual conc. 0.01 ppb to 0.80 ppb; median conc. 0.32 ppb	Packing materials were not specified.	Rosborg et al 2005
Four brands of bottled water from Greece	individual conc. 0.005 ppb to 0.06 ppb; average value 0.02 ±0.02 ppb	Packing materials were not specified.	Soupioti et al 2005
17 Softdrinks from Brazil	3 samples between 1.95 ppm and 4.11 ppm (!). All other below the detection limit.	All samples were packed in PET bottles. Detection limit not given! Antimony concentrations in the PET bottles are in the range of 25 ppm to 138 ppm.  NOTE: The values are by a factor 1000 higher than all other values. Most probably the concentrations should be 1.95 ppb and 4.11 ppb, not ppm!	Zucchi et al 2005
Citrus flavoured softdrinks	Individual conc. in PET 0.24 ppb to 1.05 ppb (n = 35), cardboard: 0.07 ppb (n = 4), glass: 0.28 ppb to 0.30 ppb (n = 3), aluminium: 0.24 ppb to 0.56 ppb (n = 3)	Samples bottled in glass, cardboard, PET and aluminium cans	Hansen and Pergantis 2006
15 Mineral water brands from Canada and 48 brands from Europe	Individual conc. Canada: 0.11 ppb to 0.38 ppb (n = 21), Germany: 0.25 ppb to 0.55 ppb; Median from Europe: 0.34 ppb (n = 35)	Bottled water in polypropylene showed significantly lower antimony concentrations. Three brands were stored for additional three months at room temperature and the antimony migration increase from 0.36 ppb to	Shotyk et al 2006

Investigated samples	Determined antimony concentrations	Remarks	Reference
		0.63 ppb.	
128 Mineral water brands from 28 countries	Individual conc. Japan: 0.01 ppb to 1.52 ppb, median conc. 0.22 ppb (69 brands from 16 countries), highest conc. 2.57 ppb (brand from Peru)	In most of the cases, the samples were stored for six months at room temperature.	Shotyk and Krachler 2007
16 Spring water, 8 mineral water and 5 tap water samples from Croatia	Individual conc. 0.02 ppb to 0.51 ppb	All samples were packed in plastic containers, the polymer types were not given.	Fiket et al 2007
189 Brands of bottled drinking water from Turkey	Individual conc. between trace amounts and 5 ppb	The packaging materials were not specified.	Güler 2007
PET bottles from Japan and China	Individual conc. 0.85 ppb to 4.40 ppb (n = 9)	0.1 g PET in 2 g water stored for 30 d and 45 d at 40 °C.	Takahashi et al 2008
Nine brands of bottled water from the United States	Individual conc. 0.10 ppb to 0.52 ppb, average conc. 0.20 ±0.12 ppb (initial), 0.23 ppb ±0.16 ppb (3 months at 22 °C), 7.8 ppb to 9.7 ppb (48 h at 80 °C), 2.1 ppb to 3.1 ppb (6 h UV irradiation)	All samples were packed in PET bottles. Migration kinetics data are given.	Westerhoff et al 2008
15 Bottled mineral water samples from Turkey	Individual conc. below the analytical detection limit of 1 ppb	Samples drawn in 2003. The packaging materials were not specified.	Baba et al 2008
Water, juices and acidic fatty food from Brazil, Argentina and	Individual conc. softdrinks: 0.16 ppb to 1.58 ppb (n = 24), juice: 0.54 ppb to 0.85 ppb (n = 3), acidic fatty food: 0.75 (n	All samples were packed in PET bottles. Data for HDPE and PP are below the analytical detection	Soares and Saiki 2009

Investigated samples	Determined antimony concentrations	Remarks	Reference
Portugal	= 1), water: 0.41 ppb to 0.85 ppb (n = 8)	limits.	
10 Brands of non-carbonated and carbonated mineral water from Hungarian	Mean conc. for non-carbonated water 0.26 ±0.16 ppb (n = 37), carbonated water 0.40 ±0.22 ppb (n = 29), highest conc. 0.8 ppb. Highest conc. 2 ppb after storage from 72 h at 60 °C.	All samples packed in PET bottles. Data for storage at higher temperatures and under daylight exposure as well as migration kinetics data are given.	Keresztes et al 2009
132 Brands of bottled water from 28 countries	Individual conc. 0.001 ppb to 2.57 ppb, median conc. 0.33 ppb	All water samples were packed in plastic (mainly in PET)	Krachler and Shotyk 2009
42 Juice samples of 16 different brands from Greece, Denmark and Scotland	Individual conc. 0.01 ppb to 13.6 ppb (n = 42)	Samples packed in glass, PET bottles and cardboard. Juices were mainly red fruits juices (black currant, raspberry, sour cherry, mint and synthetic caramel). The highest concentrations of antimony found in the investigated juices samples are coming from one brand (black currant, 16 samples of this brand were analysed, 13 in PET, 3 in cardboard). The highest antimony concentration found in the study was 13.6 ppb for a sour cherry juice produced in Greece and sold in a glass bottle.	Hansen et al 2010
294 samples of bottled water (predominantly mineral water) sold in	median conc. (PET) 0.33 ppb (n = 294), median conc. (glass) 0.02 ppb (n = 294), highest conc. (PET, distilled water, 150 d storage) 0.27 ppb (n = 126), highest conc.	294 pairs of water sold in PET as well as in glass were directly compared. Subsequently the bottles were filled with purified	Reimann et al 2010

Investigated samples	Determined antimony concentrations	Remarks	Reference
the European Union	(glass, distilled water, 150 d storage) 0.45 ppb (n = 126), median conc. (glass, distilled water, 150 d storage) <0.002 ppb (n = 126)	water. Migration kinetics data are given. Also some glass bottles leach antimony.	

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Table 3: Diffusion coefficients of antimony in PET

Temperature [°C]	Diffusion coefficient [cm <sup>2</sup> s <sup>-1</sup> ]	
	this study	Alt et al (2008)
45		1.4 10 <sup>-16</sup>
60		1.0 10 <sup>-15</sup>
75		9.1 10 <sup>-15</sup>
90		2.7 10 <sup>-13</sup>
105	3.8 10 <sup>-14</sup>	4.7 10 <sup>-12</sup>
120	1.4 10 <sup>-12</sup>	3.0 10 <sup>-11</sup>
130	2.7 10 <sup>-12</sup>	
135		2.5 10 <sup>-10</sup>
140	7.5 10 <sup>-12</sup>	
150	3.3 10 <sup>-11</sup>	3.0 10 <sup>-9</sup>

Equation 1:  $\frac{m}{A} = 2c_{P,0} \sqrt{\frac{Dt}{\pi}}$



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6 Equation 2:  $D_p = D_0 e^{-\frac{E_A}{RT}}$   
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11 Equation 3:  $\frac{m_{F,t}}{A} = c_{P,0} \rho_P d_P \left( \frac{\alpha}{1+\alpha} \right) \left[ 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} e^{\left( -D_p t \frac{q_n^2}{d_P^2} \right)} \right]$   
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18 Equation 4:  $\alpha = \frac{V_F}{K_{P,F} V_P}$   
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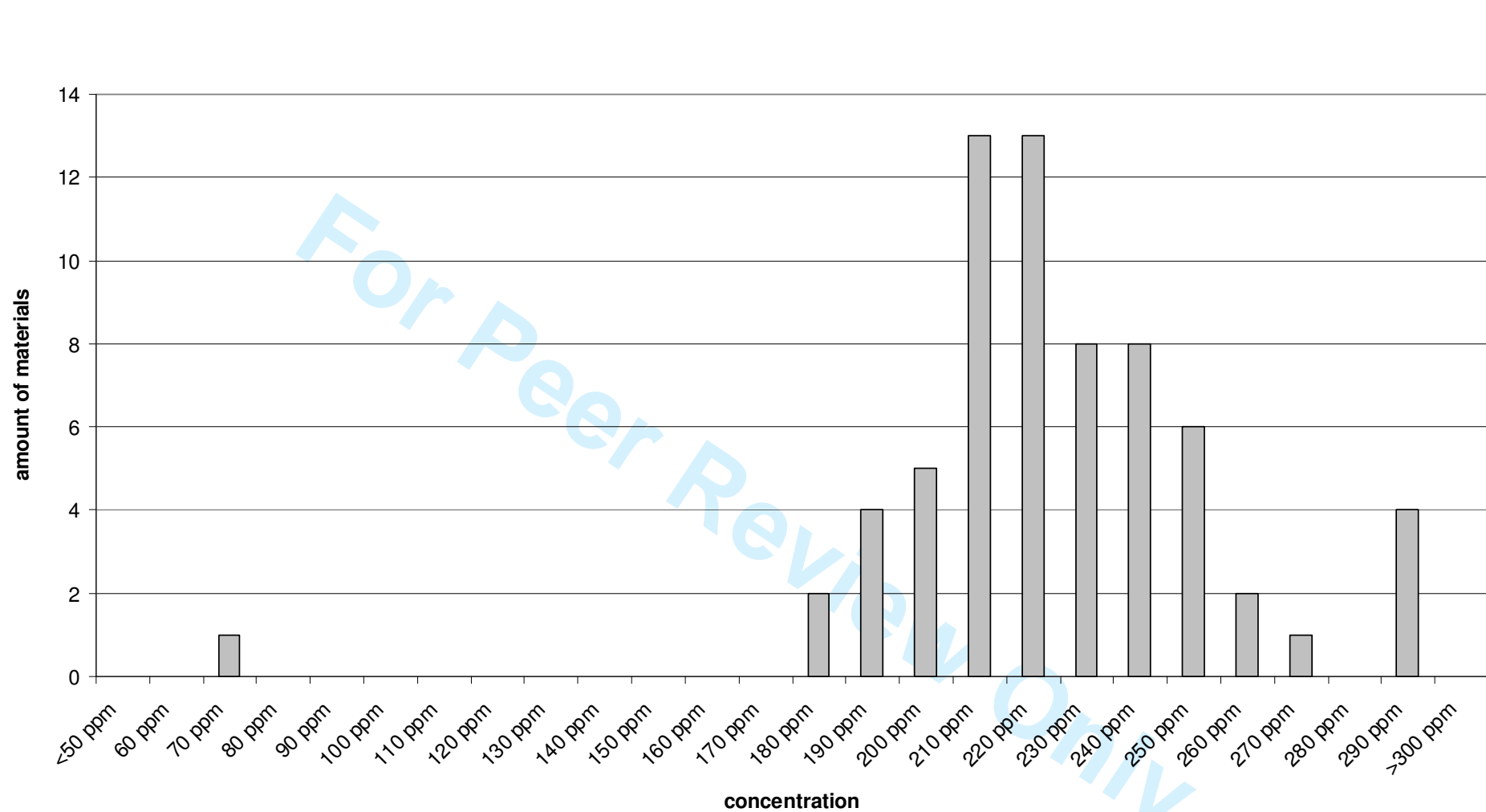


Figure 1: Antimony concentrations in PET beverage bottles and preforms from the European market (n = 67)

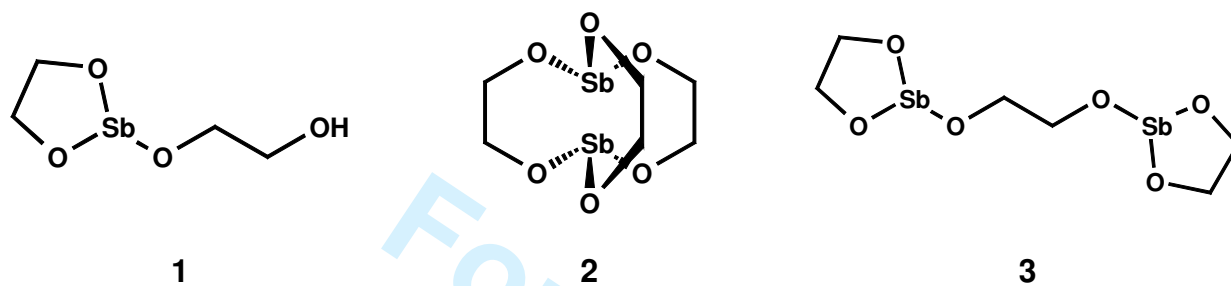


Figure 2: Proposed structures for the antimony species in PET

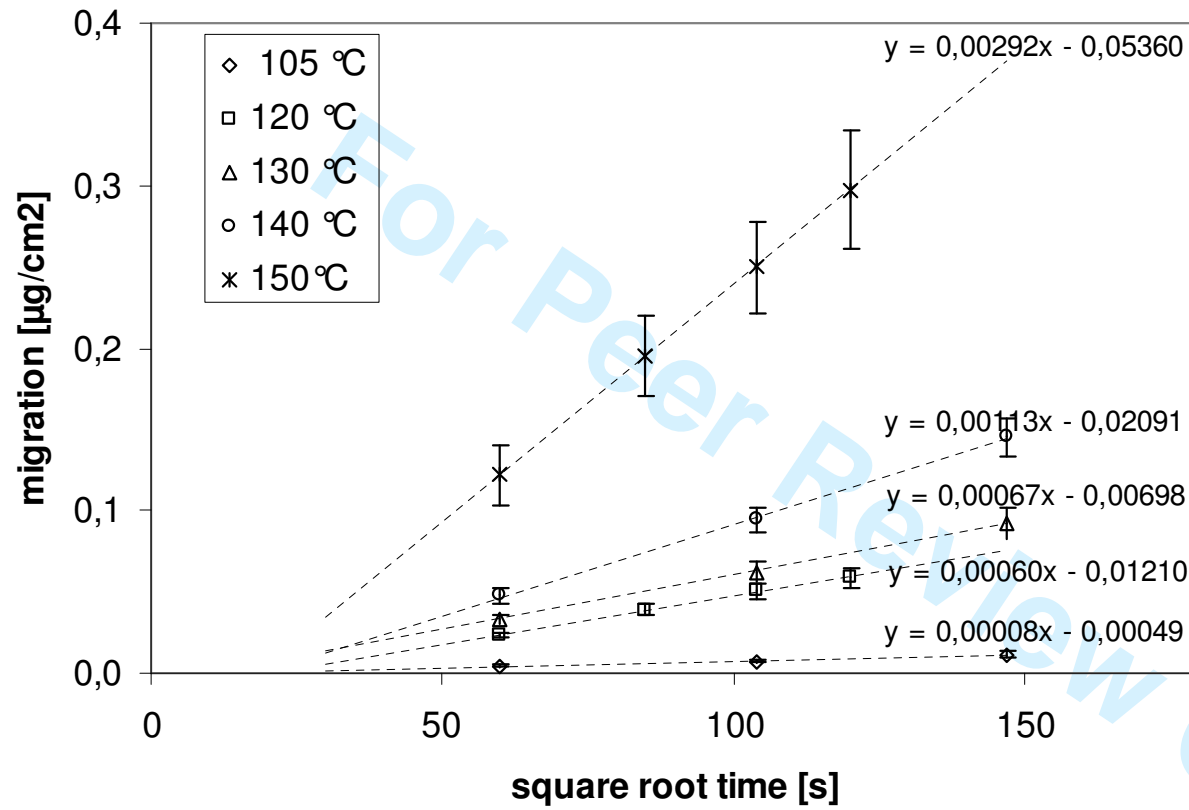


Figure 3: Migration kinetic of antimony from PET bottle into 3% acetic acid (Büchi Speed Extractor,  $c_{P,0} = 260$  ppm,  $A = 51.62$  cm<sup>2</sup>,  $V = 40$  ml)

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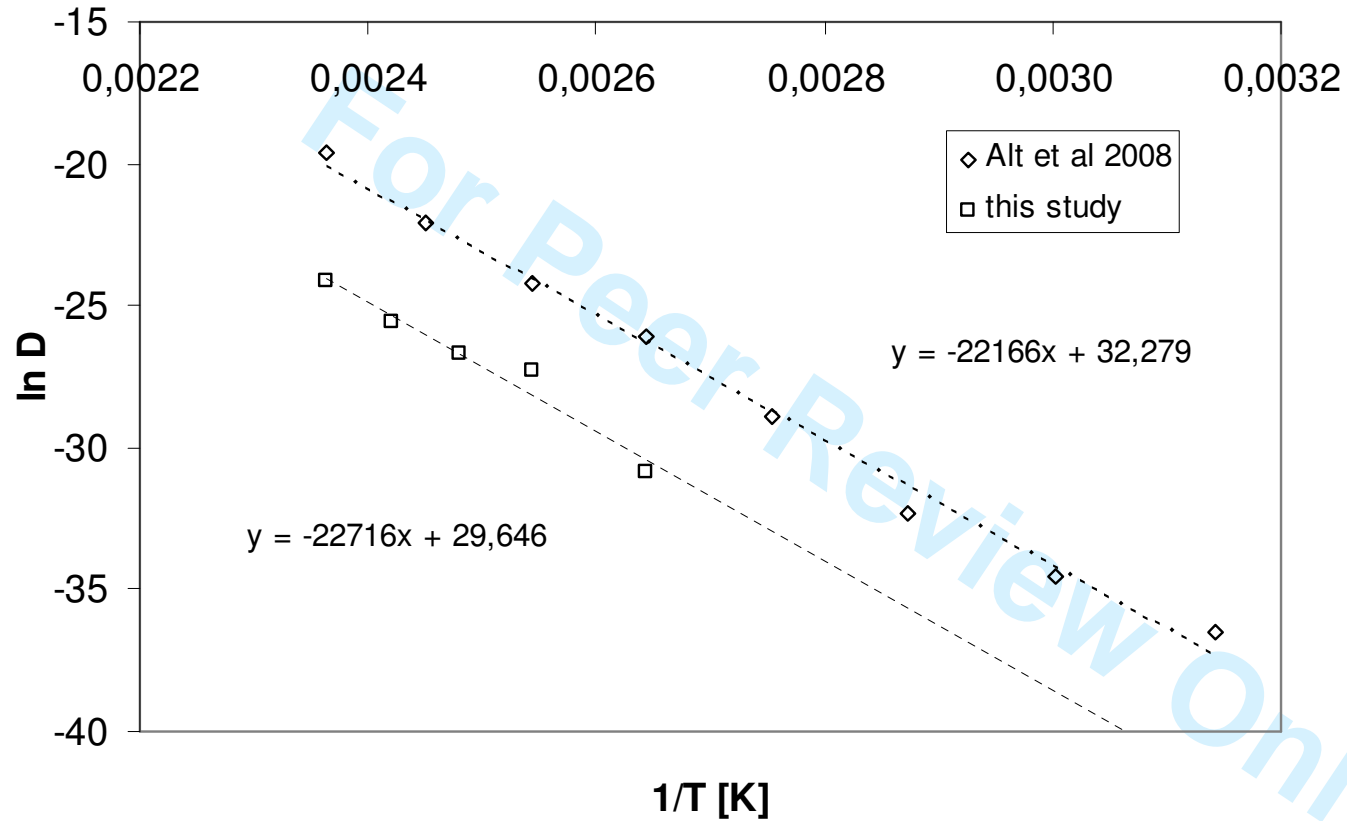


Figure 4: Arrhenius plot of the diffusion coefficients of antimony in PET (Diffusion coefficients from Table 3)

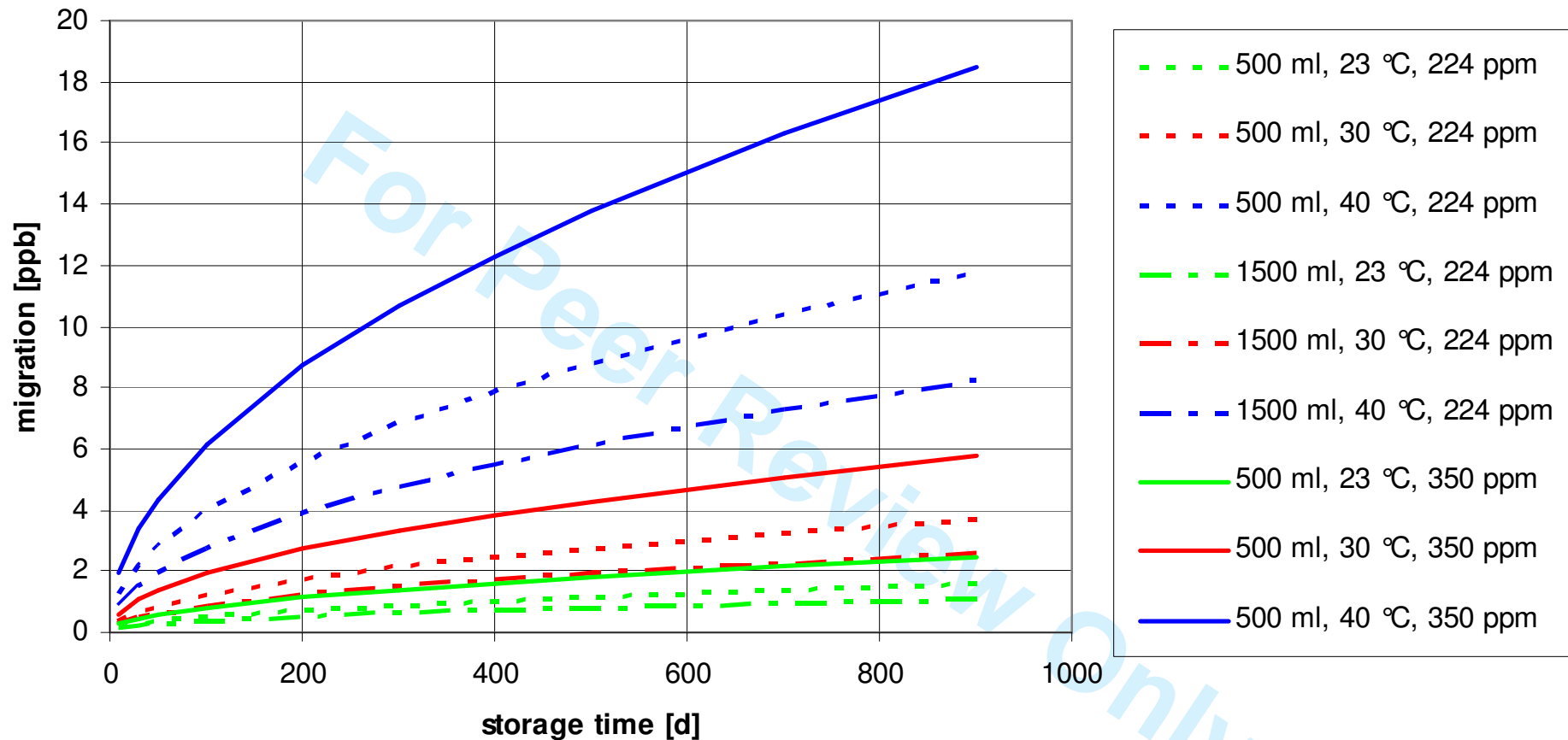


Figure 5: Calculated migration from the PET bottle into beverages as a function of the storage time and storage temperature (bottle wall concentration  $c_{P,0} = 224$  ppm and 350 ppm, activation energy  $E_A = 184$  kJ mol<sup>-1</sup>,  $D_0 = 1 \cdot 10^{14}$ ,  $K = 1$ , internal bottle wall surface 420 cm<sup>2</sup> (500 ml bottle) and 880 cm<sup>2</sup> (1500 ml bottle), wall thickness  $d = 300$  μm)