

# ANALYSIS OF THE PRESENCE OF STYRENE IN PAPERBOARD

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*Master's Thesis in Chemical Engineering written under supervision of Docent  
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## ABSTRACT

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In this work, the presence of styrene in paperboard was studied. Styrene is used in the production of styrene-acrylate (SA) and styrene-butadiene (SB) latexes. SA- and SB-latexes are the most common binders used in the coating of paper and paperboard. Pigment coating with latex can improve the appearance and printability of the product, and dispersion coating can additionally bring a barrier property to the surface, e.g., grease resistance, water resistance, or air permeability. If some chemicals in the food contact material may transfer to the food, it is called migration. Currently, styrene can be used as a monomer or other starting material in food contact materials without a set migration limit. The European Commission is currently evaluating the possible establishment of a migration limit for styrene into food. Styrene may possibly be a genotoxic compound. Since styrene is a volatile organic compound, it was studied with a headspace gas chromatography, based on the method used in Metsä Board Corporation, for which this work was done. All the results are clearly below the considered possible specific migration limit. However, the method was not suitable for quantifying styrene at these concentrations. The aim of the study was to determine the amount of residual styrene in paperboard samples and to test how time, temperature and UV light affect the amount of residual styrene. The results show that the amount of residual styrene decreases over time, but UV light has insignificant effect on the amount of residual styrene.

Keywords: Food Contact Materials, Headspace Gas Chromatography, Styrene

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## ABBREVIATIONS AND DESIGNATIONS

BCTMP	<i>Bleached-chemi-thermo-mechanical pulp</i>
BfR	<i>Bundesinstitut für Risikobewertung</i>
bw	<i>body weight</i>
C.F.R.	<i>Code of Federal Regulations</i>
CTMP	<i>Chemi-thermo-mechanical pulp</i>
CAS Number	<i>Chemical Abstracts Service Number</i>
CLP	<i>Classification, Labelling and Packaging</i>
CMC	<i>Carboxymethylcellulose</i>
EC	<i>European Commission</i>
EFSA	<i>European Food Safety Authority</i>
EU	<i>European Union</i>
FAO	<i>Food and Agriculture Organization of the United Nations</i>
FBB	<i>Folding boxboard</i>
FCM	<i>Food Contact Material</i>
FDA	<i>The United States Food and Drug Administration</i>
GMP	<i>Good Manufacturing Practise</i>
GRAS	<i>Generally Recognized As Safe</i>
HPLC	<i>High Performance Liquid Chromatography</i>
HS-GC-FID	<i>Headspace – Gas Chromatography – Flame Ionization Detector</i>
IARC	<i>International Agency for Research on Cancer</i>
IR	<i>Infrared</i>
IUPAC	<i>International Union of Pure and Applied Chemistry</i>
NHFPC	<i>National Health and Family Planning Commission</i>
ND	<i>Not Detected</i>
OML	<i>Overall Migration Limit</i>
PMTDI	<i>Provisional Maximum Tolerable Daily Intake</i>
SA	<i>Styrene-acrylate</i>
SB	<i>Styrene-butadiene</i>

SFS	<i>Spectral Fluorescence Signatures</i>
SML	<i>Specific Migration Limit</i>
SUP Directive	<i>Single-Use Plastics Directive</i>
SPME-GC-MS	<i>Solid-Phase Microextraction – Gas Chromatography – Mass Spectrometry</i>
TWA	<i>Time Weighted Average</i>
UV	<i>Ultraviolet</i>
VOC	<i>Volatile Organic Compound</i>
WHO	<i>World Health Organization</i>
4-PCH	<i>4-Phenylcyclohexene</i>
4-VCH	<i>4-Vinylcyclohexene</i>

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# 1 INTRODUCTION

In 2020, EFSA (European Food Safety Authority) published a review article titled “Assessment of the impact of the IARC Monograph Vol. 121 on the safety of the substance styrene (FCM No 193) for its use in plastic food contact materials”. EFSA assessed the available data on styrene migration and health effects. According to EFSA, styrene migration in most of the foods is less than 10 ppb but can be as high as 230 ppb, especially when in contact with fatty foods or in packaging with high surface area to volume ratio. The conclusions in the article were that styrene may be harmful to people, if they are exposed to it through food contact materials, and that the subject needs to be studied more. <sup>1</sup>

The most commonly used binders in pigment coating of paper and paperboard are styrene-butadiene and styrene-acrylate latexes. The same latexes, with different mixing ratio, are also most frequently used for the dispersion coating of paper and paperboard. At present, there are no restrictions for using styrene in food contact materials. However, the article from EFSA led the European Commission to look for evidence of the possible genotoxicity of styrene. Currently, the styrene re-evaluation process is underway, and toxicity studies are ongoing. There is a possibility that there will be a migration limit for styrene into food from all food contact materials. The new possible specific migration limit (SML) of 40 ppb might be added in the 19<sup>th</sup> amendment of the Plastics Regulation. <sup>2</sup>

Paperboard is a renewable raw material, but it lacks the barrier properties, i.e., water and grease resistance, which are needed for certain types of food, when used in food packaging. A commonly used material for food packaging is paperboard coated with polymers. Simultaneously, there is regulatory action towards plastic around the world. An example of this is the SUP Directive (Single Use Plastics Directive (EU) 2019/904) in the EU. <sup>3</sup> Another example of limiting the use of plastic in consumer items is the Plastic Ban in China. <sup>4</sup> And in the United States of America several states are coercing consumers and industry to look for alternatives to plastic. <sup>5</sup> Dispersion barrier coating helps to decrease the amount of plastic



needed in the coating, compared to for example PE extrusion used commonly in food packing. Recyclability and compostability are important features these days in food packaging.

Styrene migration into food has been widely studied during the past decades, but typically the source of styrene has been polystyrene, which is a completely different material than paperboard. The investigation of styrene migration from paperboard has been found, so far, only in one study made in 2019 by Hwang et al. In that study, styrene was not detected on the 59 paperboard samples. All the 59 paperboard samples in the article were bought from the grocery shops and they were converted food packages. However, the composition of the paperboard samples was not explained, and it remains unclear how they were coated. <sup>6</sup> This article is one reason, why migration tests were not priority in this research. Instead, it was decided to examine the residual styrene in the paperboard.

The theory part of this thesis gives an overview of the laws and regulations regarding food contact materials, the paperboard production and coating, and information about styrene and analysis methods for styrene. The goal is to investigate what kinds of methods are used for measuring styrene migration and the presence of residual styrene in food contact materials. In the experimental part, the aim is to examine how much styrene can be found in Metsä Board's paperboards used for food packaging. Raw materials containing styrene are latexes, which are used in dispersion and pigment coating. The HS-GC-FID (head space - gas chromatography - flame ionization detector) is used as the analysis method, which is inexpensive, available, and provides reliable results. GC equipment is usually found in research laboratories, and GC-FID is commonly used as an analytical method of the quantification of sample. Further, the target is to test how different conditions, time, temperature and UV light influence the presence of styrene in paperboard.

## 2 PAPERBOARD AS FOOD CONTACT MATERIAL

Safe food packaging is in everyone's interest. There are also laws, regulations, and recommendations regarding the safety of packaging. A responsible supplier complies with these regulations. GMP (Good Manufacturing Practice) is followed in the manufacturing process. The traceability of raw materials and the origin of the wood fibres are important issues that guarantee safety.

### 2.1 Compliance

Compliance in business refers to following the relevant laws and regulations for the industry. It is understood to be more than just the basic rules about taxes and accounting. Being a food contact material supplier means that large, complex sets of laws must be followed to give a compliance for the products to be used in contact with food.

#### 2.1.1 EU legislation

All food contact materials in the EU must be in the compliance with the harmonised Framework Regulation. The Regulation (EC) No 1935/2004 is called the Framework Regulation which appoints general principles of safety and inertness for every food contact material (FCM). The requirement on the Framework Regulation article 3 is that the materials will not release constituent parts into food in such amounts as to endanger human health, and the composition, odour, and taste will not change in an unacceptable way. There are specific EU-regulation for some materials, e.g., plastic. This is relevant because paperboard coated with polymers is a material often used in food packaging. The EU measure is Commission Regulation (EU) No 10/2011, which also has a nickname, the Plastics Regulation. Specific restrictions are given on the use of substances, and the Plastics Regulation also sets

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rules that must be complied with to achieve compliance of plastic materials for food contact.

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Migration limits are important, and they will indicate the quality and safety of plastic materials. These limits indicate the maximum allowable migration, chemical transfer from the material to food. There is a specific migration limit (SML) for many substances listed in the Plastics Regulation. These SMLs are established by EFSA (European Food Safety Authority) based on the toxicity data of different substances. In addition to specific migration limits, there is a limit to ensure safety and quality of the plastic, and it is called the overall migration limit (OML). The overall migration limit of all substances in the plastic may not exceed 10 mg/dm<sup>2</sup> or 60 mg/kg food. <sup>7</sup>

GMP – Commission Regulation (EC) No 2023/2006 on Good Manufacturing Practice for materials and articles intended to come into contact with food applies to all food contact material operators. This regulation insists on having a documented quality management system. The regulation defines and gives instructions to monitor the quality of raw materials and the reliability of the production process, adequacy and skills of the staff, as well as arrangement of facilities and personnel equipment. There are also instructions for documentation of business processes and organizing internal and external audits. The regulation also contains guidelines for the investigation of errors and implementation of corrective measures. <sup>8</sup>

### 2.1.2 Other most relevant regulations and recommendations

BfR (Bundesinstitut für Risikobewertung) is a German Federal Institute for Risk Assessment which serves in consumer health protection. The guiding principle for BfR is to first identify the risk and then protect health. There are numerous recommendations in the BfR, but they are only recommendations. Although they are highly respected and treated almost as a law, they are not legal norms. From these recommendations for food contact materials, the BfR XXXVI is for paper and board for food contact. This recommendation contains a so-called

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positive list of additives that are permitted in food contact materials made from paper and paperboard.<sup>9</sup>

The FDA is the U.S. Food & Drug Administration whose duty it is to protect public health. FDA C.F.R. Title 21 governs food and drug. From this regulation, part 176 is for indirect food additives: paper and paperboard components. There are two main subsections, and they are § 176.170 Components of paper and paperboard in contact with aqueous and fatty foods and § 176.180 Components of paper and paperboard in contact with dry food. Both subsections contain a positive list of additives that can be used in food contact materials made from paper and paperboard. One exception is pulp, which is not mentioned in this regulation, part 176. However, pulp is covered in C.F.R. Title 21 § 186.1673 and affirmed as generally recognized as safe (GRAS) as an indirect food substance, cellulose does not have to be listed in part 176 anymore.<sup>10</sup>

GB 9685-2016 is a Chinese National Food Safety Standard: Standard for the Use of Additives in Food Contact Materials and Articles. It contains a positive list which is a list of permitted additives which can be used when manufacturing direct food contact materials and articles. The restrictions are also listed in the positive list. The National Health and Family Planning Commission (NHFPC) must always approve new additives before they can be used to manufacture food contact materials and articles in China.<sup>11</sup>

Currently, none of these laws, regulations, or recommendations forbid using styrene in food contact materials. Styrene can be used as a monomer and/or other starting material in the food contact materials without a set migration limit, as defined in Annex I of the Plastics Regulation. There are no set migration limits in any of these above-mentioned rules either. There are no quantity or migration-related restrictions for styrene in BfR. The FDA has no limitations for styrene, and in the Chinese GB 9685-2016 standard, is only mentioned that "dosage as necessary".

## 2.2 From forest to paperboard

Forests cover about a third of the earth's entire land area. The production of various paper pulps is the most important of the current chemical uses of wood.<sup>12</sup>

### 2.2.1 Paperboard production

The most common trees in Finland: spruce, pine and birch can be divided to two categories softwood and hardwood. Spruce and pine are softwood with long fibres, while birch is hardwood with short fibres. To produce paperboard, first and most important raw material is the fibre of plant cell walls: cellulose. Softwood fibres give strength properties, while hardwood fibres improve surface properties and opacity of the paperboard. Mixing these fibres produces good paperboard. All trees contain cellulose, hemicellulose, lignin, and extractives, which need to be separated to produce paperboard.<sup>13</sup>

In chemical pulping, chemicals and heat are used to dissolve and release fibres from the lignin that binds them, the process is called chemical defibration. The chemical pulp is quite pure cellulose, but the pulp still contains a little lignin. In the bleaching of chemical pulp, the aim is to remove residual lignin from the pulp. An example of the use of hardwood pulp is white paperboard types.<sup>13</sup>

Grinding and refining are basic methods in the production of mechanical pulp. With these methods, the lignin of the wood is softened with the help of heat, water, and repeated stress. There is no attempt to dissolve any components, so the yield is almost double compared to the chemical pulp. In addition to pulp fibres, mechanical pulp contains lignin and extractives. The separation of the fibrous material is only the beginning, the mechanical processing is continued until the proportion of sticks is small enough and the desired degree of fineness in terms of pulp has been achieved. An example of the application is the middle layers of paperboard types. The chemi-thermo-mechanical pulping process is the newest and spruce

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and hardwoods can be used in the process. In the CTMP process, a mild chemical treatment is added to the heated refining process. If the CTMP is also bleached, it is called BCTMP (bleached-chemi-thermo-mechanical pulp). CTMP and BCTMP pulps are used especially for the middle layers of paperboard.<sup>13</sup>

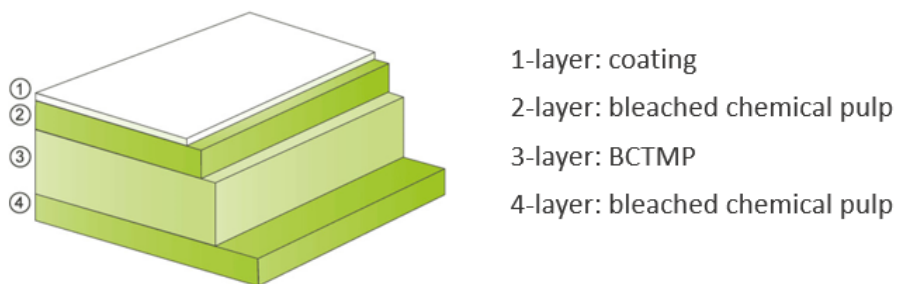
After pulp mill the pulp continues to the paperboard mill, where it is mixed with water. Then this water-pulp-suspension continues its way to the board machine. Board machine's width is several meters and the length several tens of meters. Main parts of the board machine are headbox, wire section, press section, and drying section. The web formation consists of a head box and a wire section. The head box consistency is often 0.5% and the proportion of water is 99.5%. Good formation does not contain flocks, and it improves strength properties, printability, and appearance. The different layers of the paperboard can be made with separate head boxes or multilayer head boxes.<sup>13</sup>

With the wire part, water is removed from the web by filtering it through the wire fabric. The retention, which describes the ratio of fibre and filler left on the wire to the substance fed to it, is very important in the board machine. The higher the retention is, the lower the number of foreign components is that circulates with water first in short and then in long white-water system.<sup>14</sup> All types of paperboards are characterized by the fact that the product's structural properties are already determined by the wire part. At the end of the wire section, the web contains 20% pulp and 80% water.<sup>13</sup>

The dry matter content increases by about 50% with pressing section. Due to economic reasons, it is important to remove as much water as possible in the press section, the steam used in the drying part is valuable. In the drying section, water is removed from the web with steam-heated cylinders. Pressing the wet web with the drying part also somewhat improves the bursting strength of the paperboard. As the water evaporates from the web, it starts to shrink and the hydrogen bonds that hold the paperboard together start to form. The hydrophilicity of cellulose-containing substances is due to the ability to form hydrogen bonds.<sup>14</sup> The drying part consumes a lot of energy. After this section, the dry matter content of the paperboard is approximately 95%.<sup>13</sup>

### 2.2.2 Folding Boxboard - FBB

FBB is the most common type of paperboard in Finland; it has three layers, sometimes even four. The top and back layers are bleached chemical pulp, the middle layer is mechanical pulp, or chemi-thermo-mechanical pulp (CTMP), and the middle layer often also contains machine broke. These materials in the middle layer provide stiffness. Folding boxboard has different variants, and the above-mentioned outlining is only a generalization, as each paperboard manufacturer can use their own version to produce folding boxboard. Mechanical pulp and CTMP can also be bleached, then they are called bleached mechanical pulp and BCTMP. The main purpose of the described folding boxboard is food packaging.<sup>15</sup> In Figure 1 can be seen an example of the FBB structure.



**Figure 1.** The structure of FBB. (Figure: Metsä Board)

Converters and end product users require different characteristics from paperboard. The most important characteristics have become the paperboard's strength properties, suitability for food, paperboard printability and packaging qualification. The suitability for food means that the paperboard meets the requirements of the laws on food contact materials and the hygienic cleanliness of the paperboard, which depends on the purity of the raw materials. In terms of hygienic properties, bleached pulp fibre is the best, meaning it does not contain heavy metals, other impurities, or microbes.<sup>16</sup>

The end use affects whether the FBB is left uncoated, coated with single or double layers on the top, or double-coated on the top and single-coated on the back. The surface properties of FBB are very important because it is used for demanding packaging. Among the surface properties, smoothness and surface roughness are the most important. In addition to food packaging, FBB is often used for packaging cosmetics, medicines, pastries, and cigarettes. Some FBB species can be made into postcards. The MG (machine glazed) cylinder, i.e., Yankee cylinder, combined with the folding boxboard machine improves the smoothness and closes the surface structure, which improves the coating process.<sup>15</sup> An example of a typical package made of folding boxboard is presented in Figure 2.



**Figure 2.** An example of a package made of folding boxboard - FBB.



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## 2.3 Coating of paperboard

The printability of paperboard can be improved with pigment coating, whereas dispersion coating is often used as barrier coating. High-quality boards are coated. Some advantages that can be achieved with pigment coating are decreasing of ink absorption and stiffness, increasing of gloss, surface tension, opacity, and brightness possibly, which all improve the appearance. The scale of these benefits largely depends on what kinds of components are used and how much. Water is always the diluent, binders are usually SA- and SB-latexes, and examples of fillers are kaolin, talc, and polymer particles. Same latexes are used in pigment coating and in dispersion coating, but with different mixing ratio. Especially when it comes to binder, the more binder there is, the denser the coating is, so barrier properties are achieved.<sup>17</sup>

Different applications need different amounts of coating layers, or not at all coating; the on-line and off-line coating sections differ. Each coating layer must be dried before adding anything else. Often the drying mechanism in the paperboard coating section is infrared (IR) drying. The advantage with IR is the high energy per unit area. The efficiency and the operation temperature depend on the IR unit's design along with moisture content, coating materials, and thickness of the sheet.<sup>18</sup>

### 2.3.1 Latexes

The word latex originates from the Latin verb meaning to milk. Most latexes resemble milk. Latex refers to water-borne emulsion polymers stabilized with surfactants, in which there are small polymer particles mixed with water. The reasons behind the growing interest in using polymer dispersions as barrier coatings on paper and paperboard are tightened environmental legislation, the increase of environmental awareness, and improvement of the barrier properties of dispersions.<sup>19</sup>

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The SB-latex contains typically minor impurities in ppm quantities, e.g., products of side reaction, like 4-phenylcyclohexene (4-PCH) and 4-vinylcyclohexene (4-VCH).<sup>20</sup> There are also traces of unreacted starting material, like ethylbenzene (C<sub>8</sub>H<sub>10</sub>) which acts as a starting material for styrene in a dehydrogenation process.<sup>21</sup>

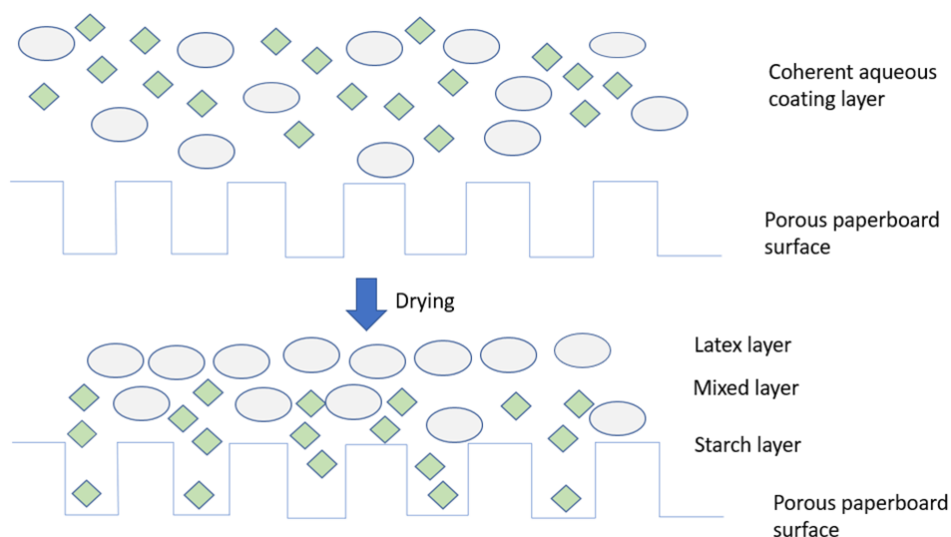
Factors influencing the popularity of latexes are bond strength, ease of use, and homogeneity. Of the latexes, SB-latex is the most used for barrier dispersions. In general, SB-latex contains 60 ± 15% styrene and 40 ± 15% butadiene. SB-latexes are commonly produced by emulsion polymerization reaction, which means a free radical polymerization of vinyl monomers in water with the surfactants present. Monomer and emulsifier concentrations, temperature, and the quantity of free radicals affect the polymerization rate.<sup>22</sup> Sunlight causes SB-latex to yellow, which is due to the breakage of double bonds, but the thermal oxidation occurs mainly in the butadiene blocks.<sup>23</sup> The gloss and hardness of the surface is improved by adding styrene, while the addition of butadiene brings softness and flexibility to the surface.<sup>13</sup>

Styrene is a liquid that polymerizes quickly. The boiling point of styrene is 145°C and the boiling point of butadiene gas at atmospheric pressure is -4°C. Therefore, high pressure polymerization is essential. After polymerization, butadiene contains more reacting double bonds, which form crosslinks when they react. The glass transition temperature, T<sub>g</sub>, is the minimum film-forming temperature; below this temperature polymer chains no longer change their shape and withstand bond deformations.<sup>22</sup> The glass transition temperature ranging from -35°C to +30°C for latexes used with paperboards and the T<sub>g</sub> is adjusted by the amount of styrene.<sup>17</sup>

Acrylate latexes are odourless, bring good water resistance to the surface, and withstand sunlight without yellowing. However, properties to resist alkali and alcohol are typically low with acrylate dispersions.<sup>19</sup> There can be smell nuisance and side taste even in originally neutral acrylate latexes. This is due to the established way to use broke in paperboard producing. The unpleasant smell originates from the SB-latex polymerization reaction by-product and is called 4-PCH.<sup>17</sup> Acrylate latexes are more expensive than SB-latexes.<sup>13</sup>

Traditionally, the term binder migration has meant migration of the latex, which occurs before drying when the latex is in liquid form. When a homogeneously mixed aqueous coating layer is added to the surface of the porous paperboard and dried, the latex layer begins to rise towards the surface as shown in the Figure 3. Zhang et al. developed an alternative migration mechanism, according to them, separation of colloidal particles occurs everywhere, not only in paper or paperboard coatings during drying, but also when colloidal films are consolidated from particles of different sizes. It is generally known that the addition of water-soluble polymers such as CMC to the coating suspension reduces latex migration to the surface. Latex migration increases as the drying temperature increases. According to Zang et al. latex migration can be reduced by adding the delay between coating and drying.

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**Figure 3.** Principle of binder migration.

Latexes are normally stable dispersions of a polymer in water. If latexes are stored in appropriate tanks and water evaporation is inhibited, they can remain stable for years. Surfaces of latexes used in paperboard coating are often negatively charged, stability may decrease along with positively charged ions or polymeric molecules.<sup>17</sup>

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### 2.3.2 Pigment coating

Pigment coating is used to improve the printing properties of the paperboard. In the coating process an aqueous suspension, which is called coating colour, is added to the surface of the paperboard. The most important component of this aqueous suspension is the pigment. Examples of pigments are kaolin and calcium carbonate. The size of a pigments is very small; typically, less than 10  $\mu\text{m}$ . The second important component in pigment coating is the binder, the glue. The binder binds pigments to the base paperboard and to each other. It also fills the intermediate between pigment particles. Various polymer dispersions, such as SB-latex, are often used as binders. There are also thickeners and various additives in this aqueous suspension, along with water, naturally. <sup>17</sup>

The coating process usually has four stages. The first is the application of the coating colour on the paperboard. This can be done in several techniques, e.g., blade coating. Additional coating colour is applied and then the excess colour is removed and with blade coating this happens with a steel blade. The coated sheet will go through the backing roll and the blade, which then leaves the necessary amount of colour to the surface of the sheet. The third stage is drying. A drying unit is always after the coating unit, and there are usually 2-4 coating units. Each coating layer must be dried before adding the next layer. The last phase of the coating process is finishing the coated layers; this usually happens with calender. The calendaring improves the smoothness of the surface without decreasing the amount of bulk. <sup>17</sup>

The requirements for paperboard are mainly set by the printing method. This considerably affects the coating process, and places demands on materials used in coating colour. Different binders are used with different printing methods. Some examples are the use of SB-latex with offset printing and the use of SA-latex with the rotogravure printing method. <sup>17</sup>

### 2.3.3 Dispersion coating

In barrier dispersion coating, a latex is applied to the surface of the base track, using e.g., blade, rod, or air brush technology, to form a solid film after drying. Water which acted as a solvent is removed by evaporation, which causes the polymer particles to start coalescing to form a uniform polymer layer. The polymer particles used in a polymer dispersion coating do not normally melt but stack together. <sup>19</sup>

The intention with dispersion coating is to achieve even coating thickness rather than an even surface. Better barrier properties can be received with even coating thickness. Even coating can usually be achieved with an air brush technology, where the excess coating from the web is removed with pressurized air coming through from a narrow gap, called air knife, and the excess coating is collected. A blade coater usually causes an even surface, then the other methods, bar and rod coaters, give somewhat rough surfaces. <sup>19</sup>

Desired barrier properties with minimal coating layering would be the relation in an ideal polymer dispersion. It should also provide good runnability properties, without blocking, cleaning, or foaming. One very important operation is drying, drying the dispersion film. The properties of the dispersion film start to develop during drying, when the coalescing and merging of polymer particles occur. Higher temperatures in drying give better barrier properties, which results from a tighter packing of the polymer particles. In case the film is dried improperly, some odour or taste problems may occur. <sup>19</sup>

Important characteristics in food applications of the dried dispersion film are odour and taste. Materials that are as odourless and tasteless as possible are a necessary choice for food packaging. Strange odours usually result from improper drying, incomplete reaction during polymerization, or wrongly selected raw materials or their handling or processing. <sup>16</sup>

A wide range of packages and wrappings, both food and non-food packages, are often polymer dispersion coated. More demands on the latex components are stipulated by food packages. Some examples are odour, taste, and appearance properties. Not only barrier properties but also other film properties, such as heat sealability, recyclability and folding, are important. All these affect barrier, composting, and crosslinking properties.<sup>19</sup>

Providing certain barrier properties is the normal purpose of a polymer dispersion coating. Resistance against grease, fat, oil, water, and water vapor are the most common barrier requirements. Other wanted barriers properties are resistance against light, gases, detergents, and hydrocarbon solvents. Usually, the barrier properties are needed to protect the products in the package from the environment, but sometimes the packaging must keep possible strong aromas of the product inside the packaging and thus protect other foods and the surrounding space from them, e.g., in the freezer. Unnecessary waste and energy consumption can be avoided by striving for a controlled barrier level depending on product and packaging requirements, instead of a maximum barrier level.<sup>19</sup>

## 2.4 UV light and its usage in print media

Ultraviolet, UV, light consists of lower wavelengths than in visible light. The UV region can be divided into three parts: UVA (315-400 nm), UVB (290-315 nm), UVC (100-290 nm).<sup>25</sup>

Flexographic printing is a letterpress printing method that uses flexible and soft printing plates. Printing ink is applied with Anilox roller to the soft printing plate (cylinder). Excess ink is removed with doctor blade from the Anilox roller. The embossed soft printing plate transfers the ink to the paperboard in a nip formed with the third, hard impression roller.<sup>26</sup> It is a popular printing method, especially in the packaging industry. The printing method can be used for paperboard, corrugated board, plastic, many kinds of paper and different laminates. The surface to be printed on can be coarse or smooth, coated or uncoated.<sup>16</sup>

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Flexographic printing often utilizes UV inks. UV light causes a polymerization reaction, and it takes a fraction of a second to dry the UV ink.<sup>26</sup> The excimer radiator is a lamp that produces monochromatic light, and most often used wavelength is 308 nm.<sup>27</sup> There are also LED UV lights used for drying. Commercial applications have been on the market over ten years now. The most often utilized wavelengths are 365, 385, and 395 nm, all from the UVA region.<sup>28</sup> There are typically 4-10 printing units, and the ink layer must be dried after each unit.<sup>26</sup>

UV light can cause similar chemical reactions in several plastics as too high a temperature. The first sign of chopping of the polymer is the change of colour and later the product embrittlement.<sup>29</sup> These chemical changes are known as ionization, which means energy that can move the electron from the ground state and this way break chemical bonds. This energy generally accounts for the breaking of double bonds.<sup>30</sup> In the case of SB-latex, this energy breaks the nonconjugated double bond in butadiene.<sup>17</sup>

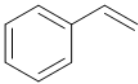
### 3 STYRENE AND ANALYSIS METHODS FOR STYRENE

Styrene, CAS 100-42-5, also known as vinylbenzene, is a volatile organic compound (VOC). Volatile organic compounds are often studied with gas chromatography.<sup>17</sup> But other methods emerged as well from the literature.

#### 3.1 Styrene

Styrene is characterized by a pungent sweet characteristic odour. It is a reactive and flammable substance that polymerizes and oxidizes easily. Most of the styrene is consumed in the production of polystyrene. According to the Chemical Product Register of the Finnish Safety and Chemicals Agency, about 14,000 tons of styrene was produced in Finland in 2016, and according to the import statistics of the Finnish Customs, about 164,000 tons of styrene was imported into Finland in 2017.<sup>31</sup> Some basic information about styrene is presented in Table 1.

**Table 1. Specification of styrene and characteristics.**<sup>31</sup>

CAS No.	100-42-5
Formula	C <sub>6</sub> H <sub>5</sub> CHCH <sub>2</sub>
Synonyms	Styrene, vinylbenzene, styrene monomer
Molecular weight	104.15 g/mol
Molecular structure	
Boiling point	145°C
Vapour pressure	0.67 kPa



According to the harmonized classification of the Regulation (EC) No 1907/2006, also known as the CLP Regulation (Classification, Labelling and Packaging), styrene is a flammable substance (H226), which is suspected of damaging the foetus (H361d), irritating the skin and eyes (H315, H319), and which may be harmful if inhaled (H332) and may damage hearing (H372).<sup>31</sup>

Concentrations known to be harmful for styrene, Time Weighted Average (TWA), have been set for concentrations in working place air. The concentrations are shown in Table 2. Styrene is also ototoxic, ear poisoning medically expressed, which can increase the harmful hearing effects of noise, if exposure occurs. Excessive concentrations of styrene in the working place air have not been detected during the polymerization of styrene or during the production or use of aqueous styrene-butadiene latexes.<sup>31</sup>

**Table 2. TWA concentration for the exposure of styrene.**<sup>31</sup>

Time	Styrene TWA (ppm)	Styrene TWA (mg/m <sup>3</sup> )
8 hours	20	86
15 minutes	100	430

Styrene was evaluated in 1984, in World Health Organization Technical Report Series 710, in the twenty-eighth report of the joint FAO/WHO (Food and Agriculture Organization of the United Nations/World Health Organization) expert committee. A comment was given by the expert committee on food additives that a PMTDI (provisional maximum tolerable daily intake) is 0.04 mg/kg bw/d (mg/kg body weight per day), and an intake of 0.004 mg/d from migration from food packaging. This was based on the available data back then that styrene may have carcinogenic activity in mice, but it had not demonstrated carcinogenic activity in rats or in humans. The absence of epidemiology studies led them accept this PMTDI on the condition that styrene migration into food had to be diminished to the lowest level technically achievable.<sup>32</sup>

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In 2019, the IARC (International Agency for Research on Cancer) updated styrene's previous evaluation from 2002. In 2002, styrene was classified as "possibly carcinogenic to humans", and in 2019 the new classification was "probably carcinogenic to humans". The IARC considered furthermore that styrene and styrene-7,8-oxide are genotoxic.<sup>31</sup> In Finland, styrene is not included in the list of chemicals that cause cancer, but its metabolic product, styrene oxide, is.<sup>33</sup>

### 3.2 Introduction to method selection

15 articles, presented in chronological order in Table 3, on styrene migration and analysis methods were reviewed. Gas chromatography with headspace was used most often, by Hwang et al.; by Varner & Breder; by Lickly et al. and by Guazzotti et al.<sup>6, 35, 37, 46</sup> and in the oldest article found, by Whitney & Collins.<sup>34</sup> A new sample preparation technique, SPME (Solid-Phase Microextraction), has been developed over the past decades and it was used, by Ling et al.<sup>41</sup> and combination with headspace method, by Naziruddin et al. and by Kontou et al.<sup>44, 47</sup>

One study with HPLC (High Performance Liquid Chromatography) was also done, by Ajaj et al.<sup>45</sup> and HPLC was recommended to be used with fatty samples by Pilevar et al.<sup>42</sup> One totally different study was made with SFS (Spectral Fluorescence Signatures), by Cvetkovic et al.<sup>43</sup> Measuring the fluorescence intensity of a sample at different emission and excitation wavelengths is the principle of SFS.

Different detectors were used in the articles listed below. FID (Flame Ionization Detector) is commonly used in quantitative measurements, while MS (Mass Spectrometry) is commonly used in qualitative measurements.

**Table 3. Review on articles of analysis methods.** <sup>6, 34-47</sup>

YEAR	Analysis method	Reference number
1978	HS-GC	34
1981	HS-GCFID	35
1994	GC-MS	36
1995	HS-GC/MS	37
2000	GC-MS	38
2005	GC-FID	39
2017	GC-MS	40
2017	SPME	41
2019	GC-MS or FID HPLC-UV or FI	42
2019	SFS	43
2019	HS-GC/MS	6
2020	HSPME-GC-MS	44
2021	HPLC	45
2022	HS-GC-MS+FID	46
2022	HS-SPME-GC- MS/MS	47

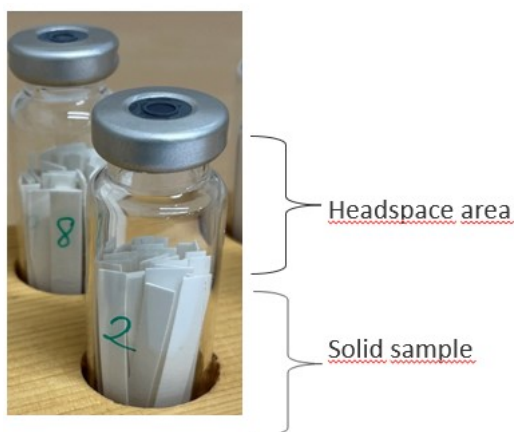
In the above listed articles styrene migration is studied with food simulants and usually from polystyrene. Although sample materials were different the substance being analysed is styrene. Food contact paperboards were studied in one article where the analysis method was comprehensive two-dimensional gas chromatography (GC-GC). In this article, it was also mentioned that there is no single analysis method which would cover all detailed requirements in analysing VOCs. <sup>48</sup>

### 3.3 Headspace Gas Chromatography

García et al. concluded that when the migrant is a volatile organic compound, such as styrene, the headspace gas chromatography technique is applicable for the analysis. <sup>49</sup>

### 3.3.1 Headspace

In connection with gas chromatography, the term headspace means the vapor phase in a closed container, vial. A closed container, a vial, also contains a gas, a solid or a liquid. Generally, the vapor is above the solid, at the top of the vial, which is where the term headspace comes from. Headspace extraction signifies the collecting and analysis of the vapor phase.<sup>50</sup> Figure 4 explains how the headspace area and the sample are placed in the vial.



**Figure 4.** Headspace vial, on the top is the headspace area, the vapor phase, and the solid sample is in the bottom, in this case paperboard slips.

The sample (gas, solid, or liquid substance) is placed in a vial and sealed immediately and tightly. The sample remains closed until it is transferred to the GC system, which guarantees the purity of the sample. The vial is thermostated at a constant temperature until equilibrium is reached between the two phases. Then, from the upper part of the vial, the headspace area, the sample is led in the gas phase together with the carrier gas to the column, where it is analyzed. This simplicity contributed to the automation of the process, which was first done by Bodenseewerk Perkin-Elmer in 1967. Automation eases the HS-GC with its only stumbling block, occasionally long equilibration times.<sup>51</sup>

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### 3.3.2 Gas Chromatography

Gas chromatography, GC, is an analytical technique developed for studying volatile compounds. From a chromatographic point of view, the most important differences in the physical properties of the mobile phase are in viscosity and diffusion properties. In gas chromatography, the interactions between the components to be analyzed and the mobile phase are minor, and the selectivity of the analysis is not affected very much by the carrier gas. If the sample is a gas, part of it can be led directly into the inert gas flow, which is also called the mobile phase or the carrier gas, taking the sample towards the column, the solid phase. If it is a liquid sample, it must first be heated so much that it vaporizes, after which the carrier gas transfers part of the vapor to the column. In the column, the sample components are separated by the selective interaction of the stationary and mobile phases. Then the different components appear at the end of the column at different times, when the detector detects them, and the data is transferred from the detector to the drawing program, which draws the characteristic analyte line, the peak, for each individual analyte. The size, height or surface area of the peaks is proportional to the number of components in the sample. The time taken for the sample to travel from one end of the column to the other is called the retention time.<sup>51-52</sup>

The main use of GC is naturally for the quantitative determination of volatile compounds in gaseous, solid, or liquid samples. The method can likewise be used for qualitative analysis. Chromatograms can be evaluated using an internal or external standard or internal normalization. In addition, a standard addition can be used, where a known amount of analyte is added to the actual sample, and the amount of the original analyte is determined from the increase in the peak area, when the area of the standard peak is already known.<sup>51</sup>

### 3.3.3 Flame Ionization Detector – FID

The most used general-purpose detector in gas chromatography is the flame ionization detector (FID). Providing an almost universal (carbon unit) response to organic compounds, low dead volume, long-term stability, a fast response, low detection limits, and exceptionally linear response range. The design of the detector defines, whether positive ions or electrons are collected. With hydrocarbons, the greatest response is achieved with FID, however it is proportional to the number of carbon atoms. A lower response is observed with compounds containing halogens, oxygen, sulphur, or nitrogen, depending on the properties of the carbon.

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The downstream end of the column is placed in the detector, while air and hydrogen gas are fed there. The effluent from the column burns with the help of hydrogen and air in a flame maintained at the tip of a metal burner. A cylindrical collector electrode is installed above the burner and an electric field is created between it and the burner. According to the working principle of the detector, the electrical conductivity of the flame changes when organic compounds are transported to the detector along with the carrier gas, linearly in relation to the amount of substance. When organic molecules burn in an oxidizing flame, electrically charged decomposition products and electrons are produced. These decomposition products are clearly visible in the current measured by the electrometer. The background current is often  $10^{-14} - 10^{-13}$  amperes, but organic compounds increase the current to  $10^{-12} - 10^{-5}$  amperes at the detection moment.<sup>52</sup>

## 3.4 Method validation

A calibration curve or standard curve as also called in analytical chemistry must be done using standards of different concentrations. In general, the peak area of the component is the response to the standard. The standard curve gives slope and correlation coefficient ( $R^2$ ). Some other important method validation items are LOD, Limit of Detection, and LOQ, Limit of Quantification.<sup>50</sup>

Limit of detection “is defined as the lowest concentration of an analyte in a sample that can be detected but not necessarily quantitated”. And limit of quantification “is defined as the lowest concentration of an analyte in a sample that can be quantitated with acceptable precision and accuracy”. Using the standard deviation in calculating of LOD and LOQ values, can be better than the estimation of mean blank signal value, especially when the concentrations are low. <sup>53-54</sup>

Calculation for LOD, based on the standard deviation of the response,  $\sigma$ , is done with following formula:

$$LOD = 3\sigma \quad (1)$$

And again, calculation for LOQ, based on the standard deviation of the response is done with the following formula:

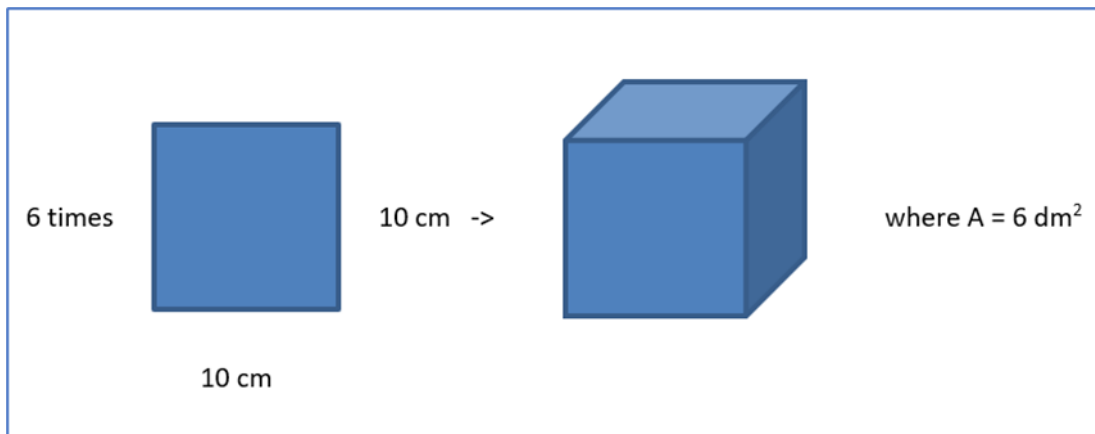
$$LOQ = 10\sigma \quad (2)$$

These presented formulas are statistical approach to determine LOD and LOQ. They can be more accurate than using the blank. <sup>54</sup>

### 3.5 Calculating worst-case migration of styrene

If migration tests are not performed with food simulants, migration can be evaluated using a worst-case calculation. In worst-case calculation it is assumed that 1 kg food would be in contact with 6 dm<sup>2</sup> surface, as well as all the residual styrene would migrate to 1 kg food.

Standard EU cube is defined in the Plastics Regulations as follows: "The food is packaged in a cubic container of 6 dm<sup>2</sup> surface area releasing the substance. The value of migration shall be expressed in mg/kg applying a surface to volume ratio of 6 dm<sup>2</sup> per kg of food. (SML [mg/kg]): the specific migration limit applicable for the substance. It is expressed in mg substance per kg food. It is indicated ND if the substance shall not migrate in detectable quantities." <sup>55</sup> The EU cube consists of square walls, where the length of one wall is 10 cm. The area of one wall is 100 cm<sup>2</sup> i.e., 1 dm<sup>2</sup>. The area of the cube formed by these walls is 6 dm<sup>2</sup> and in worst case migration calculations the cube is considered to contain 1 kg food. A demonstration of the EU cube is presented in Figure 5.



**Figure 5.** EU cube consisting of six rectangles with a side length of 10 cm.

Here is an example for worst-case migration calculation, done with variables. The variables are presented in Table 4. The last three rows are the ones being calculated; the last row shows the calculated worst-case migration result. This means, that all the residual styrene in the paperboard would migrate to the 1 kg food.



**Table 4. The worst-case migration of styrene data.**

Styrene, result from the GC (mg/m <sup>2</sup> )	a
Paperboard grammage (g/m <sup>2</sup> )	b
Paperboard grammage (kg/m <sup>2</sup> )	0.001b
EU-cube (dm <sup>2</sup> )	6
EU-cube (m <sup>2</sup> )	0.06
Styrene in paperboard (ppm)	calculated in Step 1
Styrene in paperboard (ppb)	calculated in Step 1
Calculated worst-case migration of styrene (ppb)	calculated in Step 2

Step 1, Calculating styrene content in paperboard, ppm and ppb values.

$$\frac{a \frac{\text{mg}}{\text{m}^2}}{b \frac{\text{g}}{\text{m}^2}} \cdot 1000 \frac{\text{g}}{\text{kg}} = \frac{1000a}{b} \frac{\text{mg}}{\text{kg}} = \frac{1000a}{b} \text{ ppm} \quad (3)$$

$$= \frac{a \cdot 10^6}{b} \text{ ppb}$$

Step 2, Calculating worst-case migration, based on the assumption that 1 kg food would be contact with 6 dm<sup>2</sup> surface.

$$\frac{a \cdot 10^6}{b} \frac{\mu\text{g}}{\text{kg}} \cdot 0.001b \frac{\text{kg}}{\text{m}^2} \cdot 0.06 \text{ m}^2 = 60a \frac{\mu\text{g}}{6 \text{ dm}^2} \quad (4)$$

$$\rightarrow 60a \frac{\mu\text{g}}{\text{kg food}} = 60a \text{ ppb}$$

### 3.6 Specific migration conditions

Specific migration conditions are defined in the Plastics Regulation. These conditions mimic long contact times at room temperature and colder conditions. The two most often used test conditions are presented in Table 5.

**Table 5. Specific conditions for contact times above 30 days at room temperature and below.** <sup>55</sup>

Testing for 10 days at 40°C	shall cover all storage times at refrigerated and frozen conditions including hot-fill conditions and/or heating up to $70^{\circ}\text{C} \leq T \leq 100^{\circ}\text{C}$ for maximum $t = \frac{120}{2^{\frac{T-70}{10}}}$ minutes.
Testing for 10 days at 60°C	shall cover storage above 6 months at room temperature and below, including hot-fill conditions and/or heating up to $70^{\circ}\text{C} \leq T \leq 100^{\circ}\text{C}$ for maximum $t = \frac{120}{2^{\frac{T-70}{10}}}$ minutes.

### 3.7 Air Conditioning

Paperboard ageing testing is time-consuming and standards have been developed to speed up the process. Here two of them are presented. At first ISO 5630-1:1991 (E) with title: Paper and board — Accelerated ageing. The standard states: moisture sensitizes the decomposition of cellulose. Accelerated aging compared to natural aging has shown that moisture must be involved to some extent in accelerated aging. Dry accelerated aging of cellulose is not as sensitive as when moisture is present, it probably does not rank papers in order of stability as wet accelerated aging. Moist accelerated aging correlates better with natural aging. <sup>56</sup>

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The second standard is ISO 187:1990 (E) with title: Paper, board and pulps — Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples. The standard states: the standard atmosphere for testing pulp, paper, and paperboard should be  $23 \pm 1^\circ\text{C}$  and  $(50 \pm 2) \%$  room humidity. The specimens of the samples must be stored in such a way that the conditioning air can reach all their surfaces without obstacles. This helps to achieve equilibrium state with atmospheric water vapor.<sup>57</sup>

## 4 RESEARCH METHOD AND MATERIALS

The purity of styrene (CAS 100-42-5), from Thermo Scientific Chemicals, used for analysis was 99.5%. Glyceryl triacetate was used as the solvent. The carrier gas in the GC was helium.

The calibration solutions and product samples were analyzed by PerkinElmer Clarus 580 Gas Chromatograph, with SGE BP5 Capillary GC column. The GC apparatus was equipped with TurboMatrix HS 40 headspace, and the detector was FID, Flame Ionization Detector. The column specifications are listed in Table 6. The experiments were done at the Tako mill in Tampere. The parameters of the used method in this analysis were based on the method used by Metsä Board and are introduced in Table 7. The headspace settings are introduced in Table 8.

**Table 6. SGE BP5 Capillary GC column specifications.**

Stationary Phase	5% Phenyl/95% Dimethyl Polysiloxane
Film Thickness	0.25 µm
Diameter (Metric) Inner	0.25 mm
Length (Metric)	30 m
Polarity	Nonpolar
Temperature Range	-60°C to +320/340°C

**Table 7. Method used with analysis.**

Oven Ramp	Rate (degree/min)	Temperature (°C)	Hold (min)
Initial	0.0	60	3.00
1	3.0	115	0.00
2	8.0	220	7.00

**Table 8. TurboMatrix HS 40 headspace settings.**

Vial oven	100°C
Transfer line	140°C
Needle	140°C
Thermostat	30 min
Pressurize	1.5 min
Withdraw	0.2 min
Inject	0.08 min
GC Cycle	48.0 min

In the experimental part, three of Metsä Board's paperboard grades were investigated. They represent grades with different amount on latex in their coating.

Products:

- Paperboard A, uncoated
- Paperboard B, 2-side coated
- Paperboard C, 1-side coated

Paperboard A is uncoated FBB. Both top and back layers are made of bleached chemical pulp, and the middle layer of BCTMP. Paperboard B is pigment coated on the top side and dispersion coated on the back side. Both top and back layers are made of bleached chemical pulp, and the middle layer consists of BCTMP. Paperboard C is pigment coated on the top side. Both top and back layers are made from bleached chemical pulp, and middle layer from BCTMP.

Product samples were collected from different mills and sent to Tako mill. The samples were wrapped in aluminium, except Paperboard B, which came packed in a cardboard box. All the samples were fresh, produced in January 2023. The samples were stored at room temperature, in aluminium wrapping.

## 5 EXPERIMENTS

The calibration curve was run in the beginning, with external standards of 100 pp, 50 ppm, 20 ppm, 10 ppm and 5 ppm, before product samples. However, these standards were too high concentrations. None of the product sample results corresponded to such high concentrations. The calibration curve was run again, and this time with external standards of 1 ppm, 2 ppm, 5 ppm, 7 ppm and 10 ppm. Quantification was done according to the calibration curve that was run at the latter time. The styrene with purity of 99.5% was first weighed to volumetric flask, and then it was made into a 100 ppm solution. Then this solution was diluted to the other wanted standard solutions. And the unit was calculated to change to  $\text{mg}/\text{m}^2$  which is commonly used with the gas chromatograph in Tako mill laboratory when analysing paperboard samples. The styrene concentrations at the latter time are presented in Table 9.

**Table 9. Calibration of GC method for styrene.**

Calibration solution c	Concentration of styrene (mg/ml)	Amount of styrene, converted unit ( $\text{mg}/\text{m}^2$ )
100 ppm	0.1015	1.0149
10 ppm	0.0101	0.1015
7 ppm	0.0071	0.0710
5 ppm	0.0051	0.0508
2 ppm	0.0020	0.0203
1 ppm	0.0010	0.0102

The volume of the volumetric flask with 100 ppm, 10 ppm, 7 ppm, and 5 ppm standard solutions was 100 ml. With 2 ppm, and 1 ppm the volume of volumetric flask was 50 ml. The sample size measured in the vial and fed to the gas chromatograph was 100  $\mu\text{l}$ . The amount of styrene converted unit was calculated to the commonly used unit in Tako mill laboratory, in this case 100 ppm standard solution, with following formula:

$$\frac{0.1 \text{ ml} \cdot 0.1015 \frac{\text{mg}}{\text{ml}}}{0.01 \text{ m}^2} = 1.0149 \frac{\text{mg}}{\text{m}^2} \quad (5)$$

Where 0.1 ml is sample size 100  $\mu\text{l}$ ,

$0.1015 \frac{\text{mg}}{\text{ml}}$  is the concentration of the standard solution, in this case 100 ppm, and

$0.01 \text{ m}^2$  is the size of the used paperboard sample,  $10 \text{ cm} \cdot 10 \text{ cm} = 100 \text{ cm}^2 = 0.01 \text{ m}^2$

The experimental part was divided into two parts. First, the amount of residual styrene in the fresh product samples at the beginning was studied. From here on, the procedure for all samples were the same and was done every time. Product samples of 10 cm x 10 cm were cut to slips with dimensions 0.5 cm x 5 cm. These slips were placed into a headspace vial, the vial was closed and analyzed by HS-GC-FID. The vials with product samples heading to be analyzed by HS-GC-FID can be seen in Figure 6. Three parallel measurements were made to each sample.



**Figure 6.** GC vials heading to analysis.

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Paperboard B, 2-side coated, and Paperboard C, 1-side coated, continued with further testing in the second test round. The Paperboard samples were kept under conditions where specific migration during long time storage is tested according to the Plastics Regulation and then tested. Product samples were kept 10 days in the oven first at 40°C and the second samples were kept 10 days in the oven at 60°C.

The main reason for air conditioning of paper and paperboard is to control the moisture content. In this work air conditioning is used for accelerated ageing of cellulose. Two standards were employed in this study. Air conditioning was tested with different time frames, from one day until five weeks. The paperboard samples were able to contact air without obstacles and no pretreatments were done. The test conditions are straight from the International Standard ISO 187:1990 (E). In standard conditions temperature in the room is  $23 \pm 1^\circ\text{C}$  and humidity ( $50 \pm 2$ ) %. One unfortunate set back was that the air conditioner broke, less than three weeks after the beginning of the second test round. Despite the repair attempt, the device could not be fixed. The temperature remained at 23°C in the air conditioning room for the whole time, but the humidity was only around 20%.

To find out how UV light affects the release of styrene in the paperboard samples, the samples were exposed to UV light. First, the product samples were cut to slips and closed to the GC vials and exposed to the UV light with different wavelengths and with different times. Some of the vials were exposed to UV light for one minute, and then the vials were turned 180 degrees and exposed again for one minute. The UV lamp used in the experiment had two wavelengths, 254 nm, and 365 nm. Both wavelengths were tested.

The latter wavelength is one of the used wavelengths in UV flexographic printing, with the new LED UV light technology. Because there are typically 4-10 printing units in the flexographic printing machine, and each ink layer must be dried after the printing unit, couple of the models were imitated. Here the vials were exposed to the UV light for four and five times, and then the vials were turned 180 degrees and exposed again for four and five times. The exposure imitated "the fraction of a second" drying time, by turning the UV lamp on and turning it off almost immediately. Both above mentioned turning the vials 180 degrees was



done to expose the paperboard samples in the vials as evenly throughout with UV light as possible. To gain more understanding of the effect of UV light on the presence of residual styrene in paperboard, both product samples were exposed to the 365 nm UV light for three hours. In Figure 7 can be seen some vials having an UV light exposure.



**Figure 7.** Product samples closed in the GC vials under UV lamp.

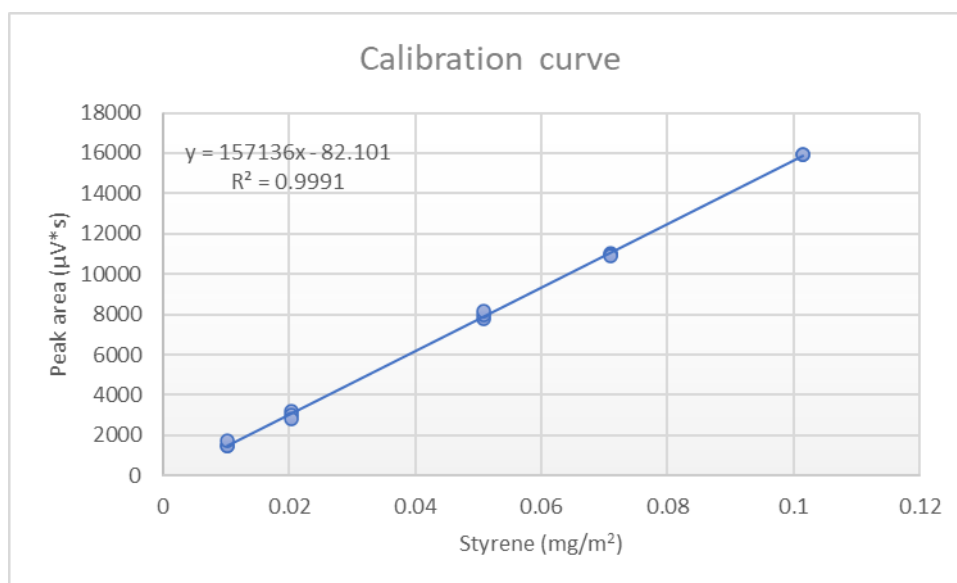
To be sure that the product samples were exposed to UV light evenly everywhere the test was repeated with changes in UV light exposures. In the second UV light testing the product samples were exposed directly under the UV lamp, with 365 nm, for two minutes and for three hours, and then the product samples were cut to slips and closed to the GC vials and analyzed by HS-GC-FID. Tests made to the paperboard samples are presented in Table 10.

**Table 10. Tests made for the samples.**

<b>Test to Paperboard samples</b>	<b>Paperboard A, uncoated</b>	<b>Paperboard B, 2-side coated</b>	<b>Paperboard C, 1-side coated</b>
Residual styrene in the beginning	X	X	X
Air conditioning		X	X
Specific migration conditions		X	X
UV-light testing		X	X

## 6 RESULTS AND DISCUSSION

In this chapter all the results will be presented, starting from the validation parameters continuing to the results of the first test round and then to the results of the second test round. The amount of styrene in the beginning, in the paperboard samples was tested in the first test round. How the different conditions, like time, temperature and effect of UV light influence on the presence of styrene in paperboard samples, were tested on the second test round. Raw materials containing styrene are the latexes, which are used in coatings. Review of the results begins with calibration curve, which is presented in Figure 8. The data of the curve is shown in Appendix A. Variations in the results may be due to the pipette, the measuring vessels, the GC, and everything the sample passes through.



**Figure 8.** Calibration curve for styrene.

The 2 ppm standard solution were run again with 20 parallel samples, and the standard deviation was calculated from the results, the data is in Appendix B. In Table 11 the used validation parameters are introduced. The data of LOD and LOQ calculations is presented in Appendix B.

**Table 11. Validation parameters for the styrene analysis method.**

LOD	0.005 mg/m <sup>2</sup>
LOQ	0.017 mg/m <sup>2</sup>

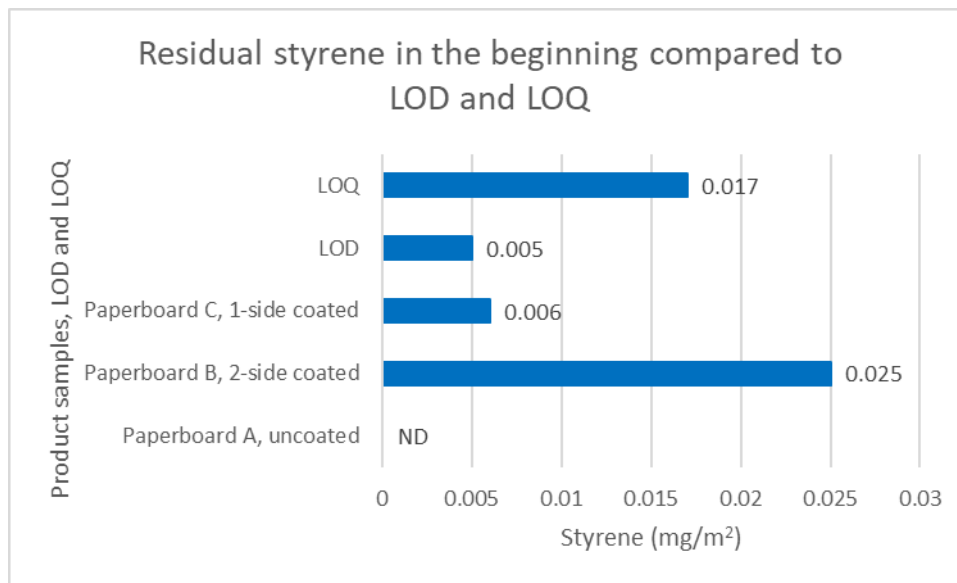
The initial state results of the samples regarding the amount of residual styrene in the beginning in the samples are introduced in Table 12. The abbreviation ND stands for not detected. The results of a comparison run for the residual state of styrene in the beginning in the product samples made by the Simpele mill laboratory are presented in Table 13. Simpele mill laboratory has HP 6890 gas chromatograph combined with Agilent G1888 headspace sampler. Their method parameters are also different compared to the used method in Tako mill laboratory. Differences in equipment and temperature program explains small differences in results. In Figure 9 the styrene's initial state results are compared to the LOD and LOQ validation parameters.

**Table 12. The residual amount of styrene in the samples in the beginning.**

SAMPLE	Paperboard A, uncoated (mg/m <sup>2</sup> )	Paperboard B, 2-side coated (mg/m <sup>2</sup> )	Paperboard C, 1-side coated (mg/m <sup>2</sup> )
result	ND	0.025	0.006
standard deviation	-	0.0005	0.0009

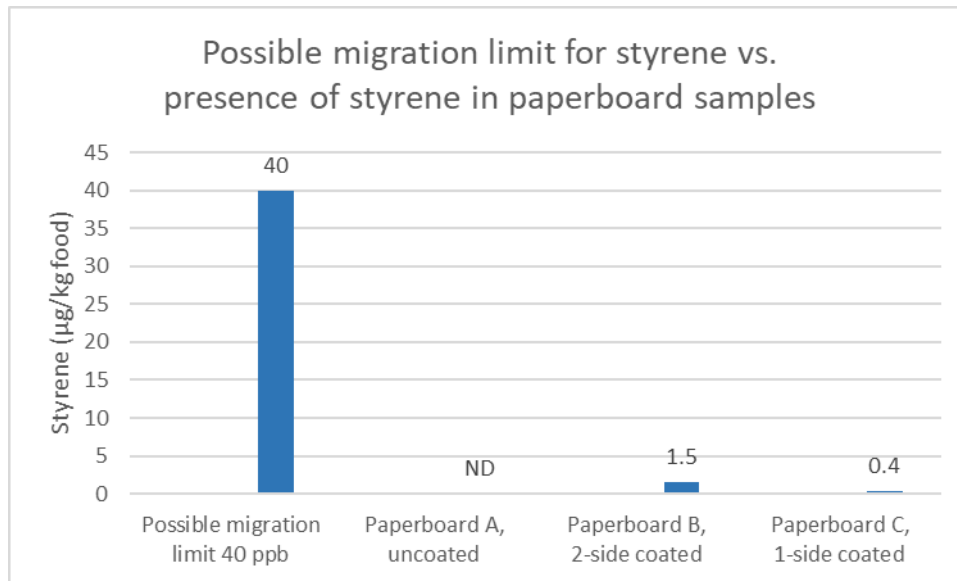
**Table 13. Comparison run from Simpele for the residual amount of styrene in the product samples in the beginning.**

SAMPLE	Paperboard A, uncoated (mg/m <sup>2</sup> )	Paperboard B, 2-side coated (mg/m <sup>2</sup> )	Paperboard C, 1-side coated (mg/m <sup>2</sup> )
result	0.001	0.021	0.009



**Figure 9.** Initial amount of residual styrene in the product samples results compared to LOD and LOQ.

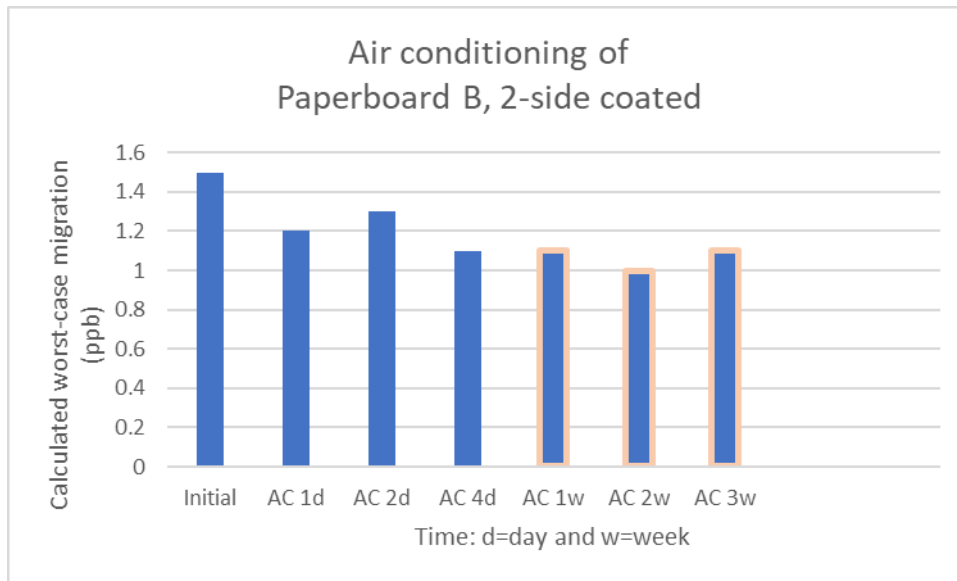
Unfortunately, the Paperboard C, 1-side coated, result is below LOQ. The result is above LOD, but this brings uncertainty to the measured results. The results for Paperboard B, 2-side coated, are above both LOD and LOQ. The review of the results continues in Figure 10, where the initial states of residual styrene in the beginning in the paperboard samples are compared to the possible specific migration limit. Because the possible migration limit is given in ppb unit, all the results are also calculated to this unit, and presented in the following tables and figures in this chapter. The results are calculated with formulas three (3) and four (4), and based on the worst-case migration assumption, meaning that all the residual styrene from the packaging (area of 6 dm<sup>2</sup>) would migrate to the 1 kg food inside. The unit µg/kg food equals to ppb.



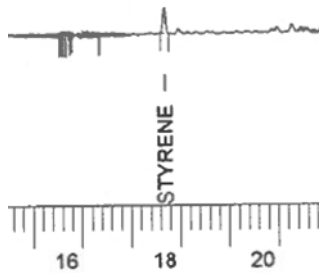
**Figure 10.** The possible specific migration limit compared to the amount of residual styrene in the beginning in the product samples. The results of the product samples are calculated to the worst-case migration assumption.

Since Paperboard B is coated on both sides it was assumed that it would contain more latex and then again, more styrene, than Paperboard C which is coated only on one side. Residual styrene ends up in the products from latexes, because of incomplete polymerization. The results in Figure 10 support for the assumption. In Paperboard A, being uncoated, was found no styrene, as can be seen in Figure 10. Other assumption is that all the residual styrene will vaporize to gas phase in the headspace area during thermostating. And in worst-case migration calculations all the residual styrene is assumed to migrate to the 1 kg food inside the packaging. The results show a very low amount of styrene, compared to the EFSA review article where was mentioned that the styrene migration is less than 10 ppb in most of the foods.<sup>1</sup> The results are also very low compared to the possible migration limit for styrene from all food contact materials to food.

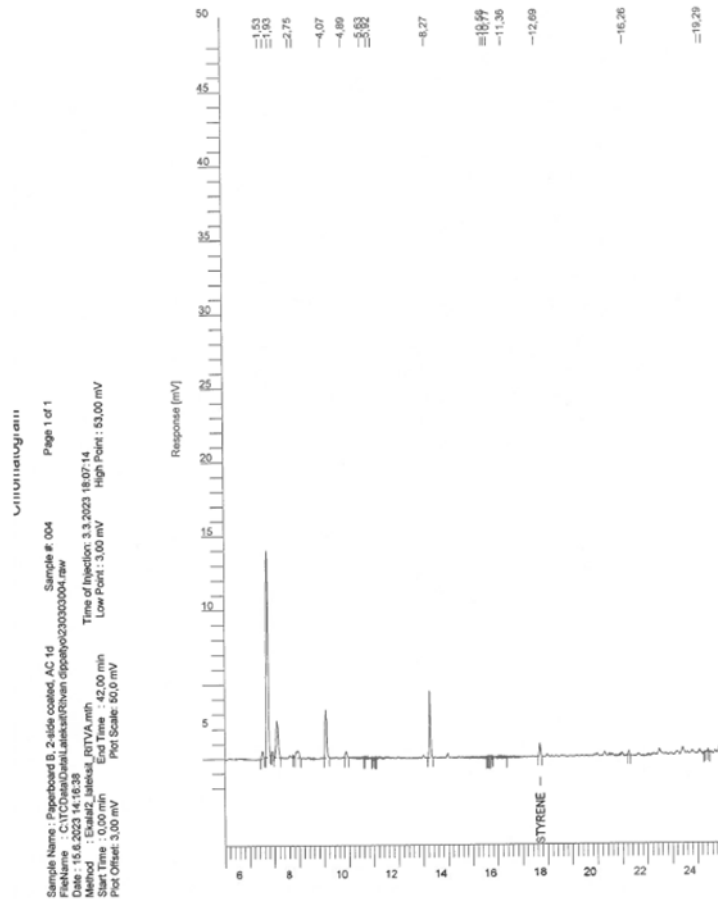
The results for air conditioning of Paperboard B, 2-side coated, can be seen in Figure 11. From the histograms, in Figure 11, can be observed that the amount of styrene diminishes during time, i.e., styrene volatilizes. The bars in the Figure 11 that are outlined with apricot colour, are affected by the air conditioner machine breakdown. Air conditioning was used for aging the paperboard samples in this work. Figure 12 shows an enlargement of chromatogram for air conditioning for one day. Figure 13 presents the original chromatogram.



**Figure 11.** Results of residual styrene after air conditioning, used for aging the paperboards, of Paperboard B, 2-side coated. Quantification was not successful for the samples of week 4 and 5.



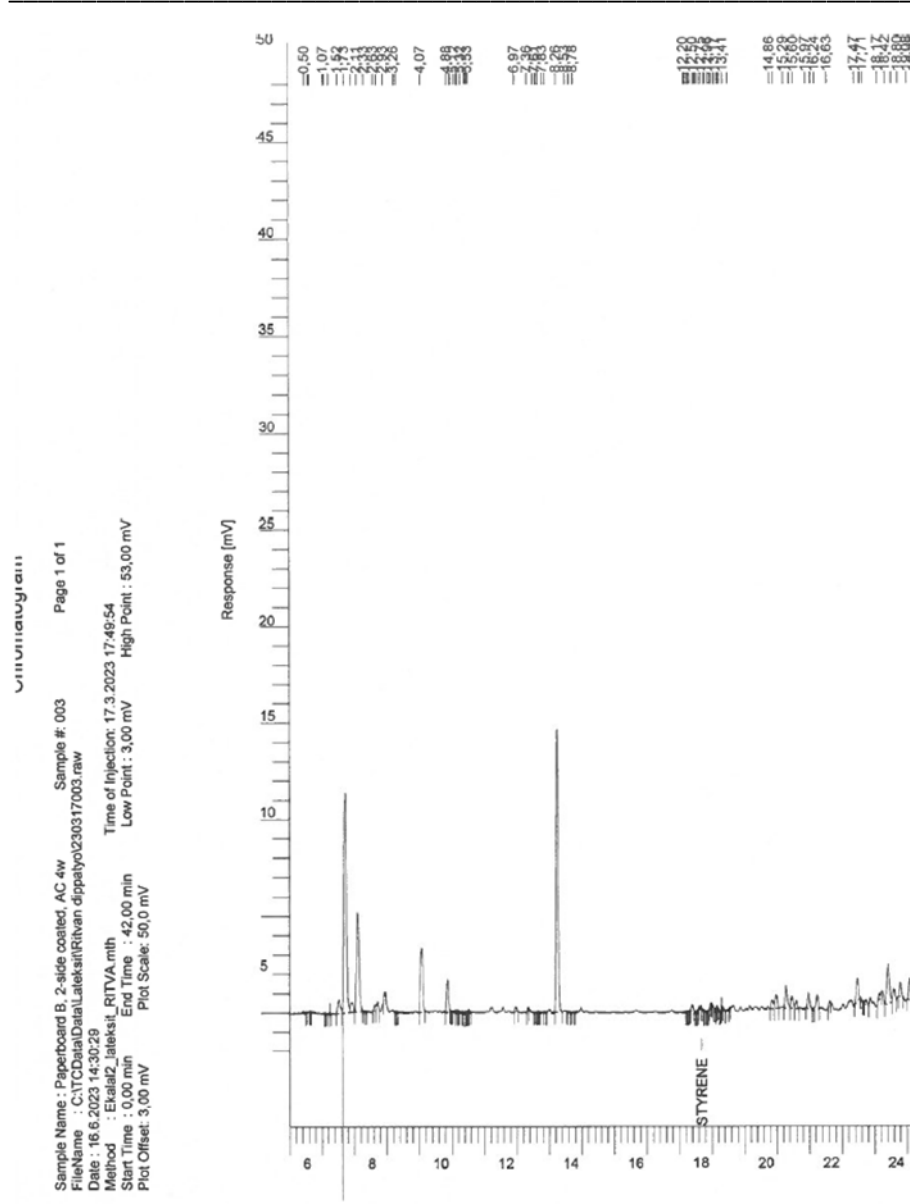
**Figure 12.** Enlargement of the chromatogram of air conditioning of Paperboard B, 2-side coated.



**Figure 13.** The chromatogram of air conditioning of Paperboard B, 2-side coated, for 1 day.

There is a clear peak in the chromatogram in Figure 12. The result for the presence of residual styrene in Paperboard B, after one day air conditioning, is  $0.022 \text{ mg/m}^2$ . When this result is calculated with formulas three (3) and four (4) based on worst-case migration assumption, meaning that all the residual styrene from the packaging (area of  $6 \text{ dm}^2$ ) would migrate to the 1 kg food inside, the worst-case migration result is  $1.3 \text{ }\mu\text{g/kg}$  food which is the same as 1.3 ppb. The results for air conditioning for 4 and 5 weeks were unclear. The gas chromatogram did recognize styrene, but due to overlapping signals, the accurate integration was impossible, as can be seen in Figure 14. It is impossible to reliably integrate such chromatograms, thus no results are reported for these samples.

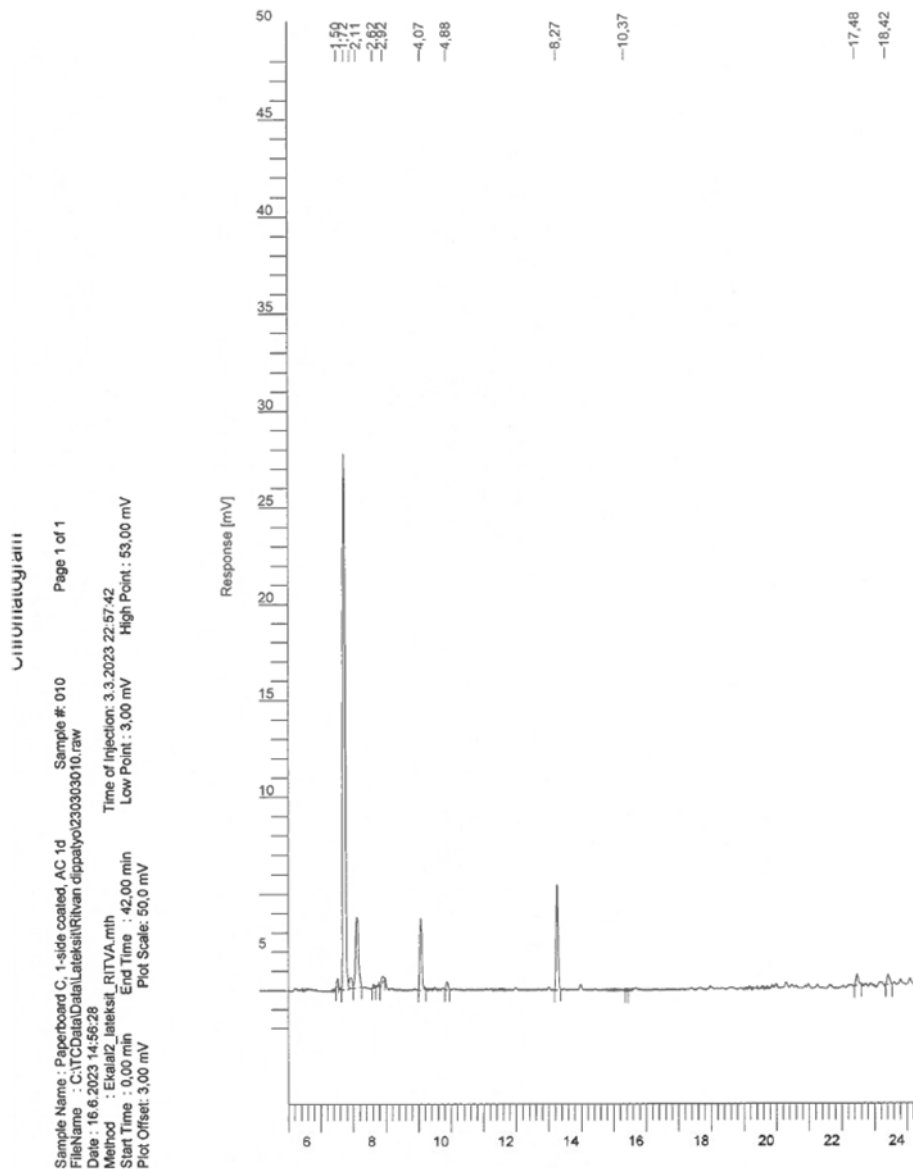




**Figure 14.** The chromatogram of air conditioning of Paperboard B, 2-side coated, for 4 weeks.

There were no detectable amounts of styrene in the samples of Paperboard C, 1-side coated.

Figure 15 shows a chromatogram for Paperboard C, where styrene is not detected.



**Figure 15.** The chromatogram of air conditioning of Paperboard C, 1-side coated, for 1 day.

The very low amount of residual styrene detected from Paperboard C in the beginning, which was also under LOQ, seems to decrease rapidly below detection limit when the paperboard is allowed to come into contact with air. All the results for Paperboard B and Paperboard C are presented in Appendices C and D.

The results for paperboard samples kept in specific migration conditions for long time storage are shown in Table 14 and Table 15 to Paperboard B, 2-side coated, and Paperboard C, 1-side coated, respectively. No food simulants were used, these were mere condition tests on paperboard. First, paperboard samples were kept in an oven at 40°C for ten days. This condition mimic storage above 30 days in refrigerator and freezer and/or heating the food. Secondly, paperboard samples were kept in an oven at 60°C for then days. This condition mimic storage above 6 months at room temperature or colder temperatures, including hot-fill and/or heating the food. The results in the middle columns are the ones that the gas chromatograph gave, and the result in the right-hand side columns represent worst-case migration result and they are calculated with formulas three (3), and four (4).

**Table 14. Results for residual styrene measured in Paperboard B, 2-side coated, in specific conditions for contact times above 30 days at room temperature and below.**

Results	Result from the GC (mg/m <sup>2</sup> )	Calculated worst-case migration (ppb)
Residual styrene in the beginning	0.025	1.5
Specific migration conditions: 40°C & 10 days	ND	-
Specific migration conditions: 60°C & 10 days	ND	-

The above results show that with Paperboard B styrene volatilizes in both cases and decreases completely or to such low concentrations that it cannot be detected.

**Table 15. Results for residual styrene measured in Paperboard C, 1-side coated, in specific conditions for contact times above 30 days at room temperature and below.**

Results	Result from the GC (mg/m <sup>2</sup> )	Calculated worst-case migration (ppb)
Residual styrene in the beginning	0.006	0.4
Specific migration conditions: 40°C & 10 days	ND	-
Specific migration conditions: 60°C & 10 days	ND	-

With Paperboard C the above results show that styrene volatilizes in both cases and decreases completely or to such low concentrations that it cannot be detected. Styrene decreases with temperature over time, which these specific conditions describe. The results are similar in both paperboard samples.

The results for residual styrene in the beginning in Paperboard B, 2-side coated, and after UV light exposure in the vials can be seen in Table 16. The results of the effect of UV light being exposed straight under UV lamp for Paperboard B can be seen in Table 17. The samples exposed straight under UV lamp, was cut afterwards to slips and closed to the vials.

**Table 16. Results for the residual styrene in the beginning and after UV light exposure in the vials of Paperboard B, 2-side coated.**

<b>Results</b>	<b>Result from the GC (mg/m<sup>2</sup>)</b>	<b>Calculated worst-case migration (ppb)</b>
Residual styrene in the beginning	0.025	1.5
365 nm 1+1 min	0.021	1.3
254 nm 1+1 min	0.02	1.2
365 nm imitation of flexo printing with 4 printing units	0.022	1.3
365 nm imitation of flexo printing with 5 printing units	0.02	1.2
365 nm 3 h	0.023	1.4

**Table 17. Results for the residual styrene in the beginning and after UV light exposure straight under UV lamp of Paperboard B, 2-side coated.**

<b>Results</b>	<b>Result from the GC (mg/m<sup>2</sup>)</b>	<b>Calculated worst-case migration (ppb)</b>
Residual styrene in the beginning	0.025	1.5
365 nm 2 min	0.017	1.0
365 nm 3 h	0.012	0.7

The measured amount of residual styrene in Paperboard B, after being exposed straight under UV light, 365 nm, for 3 hours is 0.012 mg/m<sup>2</sup> and when this result is calculated with formulas three (3) and four (4) the worst-case migration result is 0.7 ppb. From this series of measurements, only one measurement was successful and there are no parallel results for it, this in turn brings uncertainty to the reliability of the result. This one result is under limit of quantification, and the result is lower than the amount of residual styrene in the beginning, this may be a result of performing the experiment in a well-ventilated fume cupboard,

possibly promoting the evaporation of a volatile compound. The result is though above the detection limit.

The results for residual styrene in the beginning in Paperboard C, 1-side coated, and after UV light exposure in the vials can be seen in Table 18. The effect of UV light being exposed straight under UV lamp for Paperboard B can be seen in Table 19. The samples exposed straight under UV lamp, was cut afterwards to slips and closed to the vials.

**Table 18. Results for the residual styrene in the beginning and after UV light exposure in the vials for Paperboard C, 1-side coated.**

<b>Results</b>	<b>Result from the GC (mg/m<sup>2</sup>)</b>	<b>Calculated worst-case migration (ppb)</b>
Residual styrene in the beginning	0.006	0.4
365 nm 1+1 min	ND	-
254 nm 1+1 min	ND	-
365 nm imitation of flexo printing with 4 printing units	ND	-
365 nm imitation of flexo printing with 5 printing units	ND	-
365 nm 3 h	ND	-

The amount of residual styrene decreases in such a low level that it cannot be detected anymore with the used temperature program. And it is important to notice that the amount of residual styrene in Paperboard C was already under quantification limit in the beginning.

**Table 19. Results for the residual styrene in the beginning and after UV light exposure straight under UV lamp of Paperboard C, 1-side coated.**

<b>Results</b>	<b>Result from the GC (mg/m<sup>2</sup>)</b>	<b>Calculated worst-case migration (ppb)</b>
Residual styrene in the beginning	0.006	0.4
365 nm 2 min	ND	-
365 nm 3 h	ND	-

The amount of residual styrene in paperboard does not change much with different UV light exposures. It can be said, based on these measurements, that UV light has insignificant effect on the amount of residual styrene in paperboard.

Paperboard B and Paperboard C were also analyzed in Äänekoski research laboratory by SPME-GC-MS. The analysis was done to the presence of residual styrene in the beginning and after UV light exposure, straight under UV lamp. Styrene was not identified in Paperboard C analysis. The results for Paperboard B suggest that UV light has no effect on the amount of residual styrene in paperboard.

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## 7 CONCLUSIONS

Three different paperboard grades were studied to learn how much there is residual styrene in the Metsä Board paperboards. They represent grades with different amount of latex in their coating. First, the amount of residual styrene is analyzed in the original paperboard samples. No styrene was found in Paperboard A, uncoated. Paperboard B, 2-side coated, and Paperboard C, 1-side coated, continued to be tested under different conditions for the second test round. These samples were aged with air conditioning for different times, in a room where the temperature was throughout 23°C and the humidity was 43%, in the beginning. After the unfortunate air conditioner broke, the humidity was only around 20%. These two product samples were also kept in specific conditions in an oven for ten days, first at a temperature of 40°C and then at a temperature of 60°C. These specific conditions mimic common storage conditions above 30 days at room temperature and below. The effect of UV light on the presence of styrene in paperboard samples was also tested with both products.

The calibration curve was run twice. On the first time, before running any product samples, the chosen concentrations were too high. On the second time, the chosen concentrations were at a much lower level. 5 ppm and 10 ppm standards were run both times, the integrated results of the peaks were similar, and they are presented in Appendix A. The need to run a second calibration curve brings though again a little uncertainty to the results. The results of the product samples were quantified using the calibration curve obtained at the latter time.

The presence of residual styrene in the paperboard samples is low. All the results are based on worst-case migration calculations. The assumption in these calculations is that all residual styrene, in this case, would transfer to 1 kg food in the packaging, with area of 6 dm<sup>2</sup>. No food simulants were used. The results achieved fall below the possible migration limit. Styrene is a volatile organic compound and it evaporated during specific conditions and in air conditioning. However, with the breakdown of the air conditioner, the conditions were not standard conditions, so the drier air may have affected the results. Based on this research the amount of UV light did show only insignificant differences in the presence of styrene in



the paperboard. It did not matter if the samples were in the vials or directly under UV light. According to the literature UV light does cause butadiene blocks to break down, in the form of thermal oxidation, but according to the measurements, ionization does not affect the amount of styrene.

The scattering of the results may be caused, in addition to the above, for example, that the gas chromatograph was placed in a new room just before the measurements. There were new gas pipes installed in the new room. Leakage of helium gas cylinder during measurements and evenness or unevenness of gas flows may have impacted the results. Important factors are also sensitivity of the gas chromatograph and purity of the column. The results are also affected by accuracy of all used measuring instruments, pipettes, scale, and measuring glasses. And generally anything that the sample passes through.

Paperboard B, 2-side coated, results are above both LOD and LOQ, except one result from the UV light tests. Paperboard C, 1-side coated, results were already in the beginning below LOQ, but above LOD. The method used was not suitable for measuring such low concentrations, the accuracy was not enough. Poorly distinguishable and detectable chromatograms, where the peak does not separate from the baseline, were impossible to reliably integrate. Signal overlap was another matter that made integration impossible. The development of the method, to ensure the amount of residual styrene at very low concentrations and below 40 ppb will probably be necessary in the future. Or perhaps, the suitable method can be expected from the legislator. The development of the method was limited to the scope of this study. It would also be interesting to see how the particle size in latexes affects the transfer and transport of compounds to the surface and how drying temperatures affect the binder migration with used latexes, hence the presence of residual styrene in paperboard.

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## APPENDIX A – Calibration / Standard curve for styrene, data

### Calibration curve data

Amount of styrene in converted unit (mg/m <sup>2</sup> )	Area (μV*s)
0.01015	1510.96
0.01015	1508.34
0.01015	1754.29
0.0203	3170.29
0.0203	3030.22
0.0203	2822.44
0.05075	7815.97
0.05075	7969.04
0.05075	8169.80
0.07104	11002.77
0.07104	10941.72
0.07104	10931.88
0.10149	15930.73
0.10149	15954.88

For the comparison, results of the 5 ppm and 10 ppm standards, at the first time.

Amount of styrene in converted unit (mg/m <sup>2</sup> )	Area (μV*s)
0.05373	8144.92
0.05373	7991.89
0.05373	8186.6
0.10746	16220.08
0.10746	16317.47
0.10746	15700.33

## APPENDIX B – LOD &amp; LOQ data

## Method testing with 2 ppm standard solution

ppm	Amount of styrene (mg/m <sup>2</sup> )	Result from the GC (mg/m <sup>2</sup> )	average (mg/m <sup>2</sup> )	standard deviation (mg/m <sup>2</sup> )
2	0.0203	0.021		
2	0.0203	0.018		
2	0.0203	0.018		
2	0.0203	0.019		
2	0.0203	0.023		
2	0.0203	0.019		
2	0.0203	0.019		
2	0.0203	0.023		
2	0.0203	0.021		
2	0.0203	0.018		
2	0.0203	0.023		
2	0.0203	0.019		
2	0.0203	0.022		
2	0.0203	0.021		
2	0.0203	0.020		
2	0.0203	0.020		
2	0.0203	0.020		
2	0.0203	0.018		
2	0.0203	0.022		
2	0.0203	0.022		
			<b>0.0203</b>	<b>0.001734935</b>

LOD: 3\*standard deviation

LOQ: 10\*standard deviation

LOD	0.005	mg/m <sup>2</sup>
LOQ	0.107	mg/m <sup>2</sup>



## APPENDIX C– Paperboard B Results

Paperboard B, 2-side coated

Sample	Result from the GC (mg/m <sup>2</sup> )	Standard deviation (mg/m <sup>2</sup> )	µg/kg paperboard	Calculated worst-case migration (ppb)
Residual styrene in the beginning	0.025	0.0005	128	1.5
AC 1 d	0.02	0.0014	103	1.2
AC 2 d	0.021	0.0005	108	1.3
AC 4 d	0.019	0.0005	97	1.1
AC 1 w	0.019	0.0019	97	1.1
AC 2 w	0.016	0.0008	82	1.0
AC 3 w	0.019	0.0005	97	1.1
AC 4 w	ND			-
AC 5 w	ND			-
Specific migration conditions: 40°C & 10 days	ND			-
Specific migration conditions: 60°C & 10 days	ND			-
UV light, vials				
365 nm 1+1 min	0.021	0.00022	108	1.3
254 nm 1+1 min	0.02	0.0029	103	1.2
365 nm imitation of flexo printing with 4 printing units	0.022	0.0016	113	1.3
365 nm imitation of flexo printing with 5 printing units	0.02	0	103	1.2
365 nm 3 h	0.023	0.0025	87	1.0
UV light, straight				
365 nm 2 min	0.017	0.0005	87	1.0
365 nm 3 h	0.012	0	62	0.7

The rows with apricot colour are affected by the air conditioner machine breakdown.

## APPENDIX D – Paperboard C Results

Paperboard C, 1-side coated

Sample	Result from the GC (mg/m <sup>2</sup> )	Standard deviation	µg/kg paperboard	Calculated worst-case migration (ppb)
Residual styrene in the beginning	0.006	0.0009	23	0.4
AC 1 d	ND	-	-	-
AC 2 d	ND	-	-	-
AC 4 d	ND	-	-	-
AC 1 w	ND	-	-	-
AC 2 w	ND	-	-	-
AC 3 w	ND	-	-	-
AC 4 w	ND	-	-	-
AC 5 w	ND	-	-	-
Specific migration conditions: 40°C & 10 days	ND	-	-	-
Specific migration conditions: 60°C & 10 days	ND	-	-	-
UV light, vials				
365 nm 1+1 min	ND	-	-	-
254 nm 1+1 min	ND	-	-	-
365 nm imitation of flexo printing with 4 printing units	ND	-	-	-
365 nm imitation of flexo printing with 5 printing units	ND	-	-	-
365 nm 3 h	ND	-	-	-
UV light, straigh				
365 nm 2 min	ND	-	-	-
365 nm 3 h	ND	-	-	-

The rows with apricot colour are affected by the air conditioner machine breakdown.