DIPLOMARBEIT

MIGRATION FROM COFFEE FILTER PAPERS

ausgeführt am

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unter der Leitung von

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durch

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1 ABSTRACT

Coffee filter papers are a product which is used all over the world on a daily bases in countless homes and workplaces. Especially in Austria the coffee brewing is part of the daily lives of many people and using filter papers is a common method.

But as literature research showed there were no big studies done on the **migration from coffee filter papers** into coffee, neither internationally nor in Austria. Coffee brewing applies hot water to the paper for a longer period of time which is rarely the case at paper products in contact with food materials, so the possibilities of migration are much higher than at other food-paper products.

So the aim of this Diploma work is to **give a good overview of the commercial available coffee filter paper products in Austria** and to test the gathered samples on possibly **migrating substances**. The differences between the samples, the comparison to safety limits and the possible influence of bleaching were all considered.

The aim was not to focus on a few substances and go into greater detail but to test a reasonable amount of different ones and different methods to get a good overview and if some might cause concern and call for a closer look.

In the **first part** of the Diploma work the focus lied on getting as much general information on the filter paper samples like **optical comparison, weight, contact area or moisture content**.

Then the migration of substances was given a general overlook. As a simulator for coffee **coldwater and hotwater extracts** were used. There a general guidelines how to prepare and test the extracts so these were followed.

The overlook contained the **dry matter content** which gives the total amount of migrated content which does not evaporate before 100°C.
The measurement of the **pH** change the migrating substances cause in the extracts gives also an overlook if there are big differences between the samples.
Lastly to complete the general picture a method with **Potassium permanganate** was performed to determent the organic content of the migrating substances overall.

In the **second part** the amount of migrating substance was determent at some chosen chemicals or to see if certain substances are present at all.

Photometric measurements showed the migrating amount of **glyoxal, formaldehyde and pentachlorophenol**.
The **scanning electron microscope** was used to give a good overlook of visible contaminations in the filter papers.
The **Headspace-Gas chromatography-Mass Spectrometry** method was used to determent if a greater amount of any substances are present in the sample papers which are vaporable until 150°C.
With the **X-Ray fluorescence spectroscopy** a focus on the metals present in the filter papers could be drawn.
The fluorinated substances were analysed in greater detail with a **Gas chromatography Echelle Plasma Emissions Detector**.

And as a last method a **Multimethod with Gas chromatography-Mass Spectrometry** was used to determent the amount of possibly harmful migrating substances under harsher conditions than. Here the amount **pentachlorophenol** or **phthalates** were tested.

All these experiments should reach the aim of a getting the good overview and get to a conclusion if some results call for concern and maybe further studies.

2 INTRODUCTION

2.1 Overview of pulp and paper products

The pulp and paper market is a steady rising one worldwide. In Germany the paper industry is the 26. largest industry. (1)
Where the different products are divided as following: (1)

- 41,7% Graphical Papers
- 26,7% Packaging Papers
- 20,1% Packaging Cart boards and pulps
- 5,1% Sanitariness Papers
- 3,8% Technical and Special Pulps
- 2,6% Technical and Special Papers

The **Technical and Special Papers** include the papers in contact with food materials, filter papers, cigarette papers and very special paper products like condenser or photo paper .(1)
So the filter papers are a small part of a small segment of the paper industry but still a very relevant part of the daily lives of many people.

2.2 Papers in contact with food materials production

The following substances are used to create paper products designed to be in contact with food materials:

Fibre materials: (1)

- Manila
- Cellulose fibers
- Cotton wool
- Recycled paper is pushed back at papers in contact with food materials
- Materials like asbestos fibers are no longer used because of health risk reasons

Additives: (9)

- Glues
  - Strain hardening and hydrophobic effect
  - Ex.: **real glues** like Casein; **alginates**, **waxes**, **paraffins**,…
- Fixer and flocking agents
  - binding of the glue or other substances (fungicides,…) to the fibers
  - Ex.: **Aluminium sulfate**
- Dehydration accelerator
  - speeds up the production because a faster water drainage
- Retention agents
  - Agglomeration of fine which would be lost otherwise
- Flotation agents
  - Helps to create a smooth paper surface
- Foam preventing agents
  - Prevention of air bubbles
- Slime combating substances

    - In recycled water bacteria grows, these substances combat those, a limit amount of biocides is allowed at the paper production (11)
- Preserving agents
    - Protection from microbiologic dangers
    - Ex**.: Sorbic acid, Sodium- or Potassium-sorbate** (12)
    - Also gamma radiation against fungicides is possible (13)
    - **Pentachlorophenol** is mostly forbidden at paper in contact with foodstuffs (48)
- Wet compression
    - To prevent from dissolving when in contact with liquid solutions
    - Ex.: **urea-formaldehyde resin**, **melamine-formaldehyde resin** (migration problem of the monomer formaldehyde, degree of cross-linking and amount of resin are factors, **glyoxal** is also a possible contamination from resins), **polyethylene imine**, **chrome-stearate-complexes** (forbidden in the EU)
- Dyes, pigments
    - Most colouring agents can not be used because the migration potential is very high, so mostly no colouring at the direct contact area
- Brightener
    - Often forbidden or highly regulated
    - Ex.: Stilbene derivates
- Surface finishing and –coating
    - To prepare the paper for the intended food product (liquid, fatty,…)

The paper production process begins with the processing of the raw material. Either wood pulp is made at a nearby or the same factory or is delivered in wet bales. This raw material is put into a mixer with water, here the fibers are decollated. In a refiner they are grounded. Then the actual paper making process can start, here it is branched into the different products - method and additives depend on the use of the final paper like for coffee brewing. (9)

2.3 Filter papers and filter masses

Liquid foodstuffs, drinks and tobacco are filtered to enhance the taste value or the increase the durability. This is done with fixed layers which are created by the fabrication process. Sometimes the layers are supported with additives. (1)
Filter Additives: (1)

- Kieselguhr
- Activated Carbon
- Plastics

The **filter papers for coffee or tea products** are made of cellulose fibers without many additives. Made mostly with the **Sulfate or Sulfite method** sometimes also with the use of Linters. (1)

Coffee filter papers are made from creped paper. Crêpe paper is tissue paper that has been coated with sizing and then creped to create gathers. The crêping allows the coffee to flow freely between the filter and the filtration funnel. The raw materials for the filter paper are coarse long fibre, often from fast growing trees. In the end a cellulose fibre grid of under 10µm mesh width is produced.
Both bleached and unbleached qualities are made. For a filter to be compatible with a coffee maker, the filter needs to be a specific shape and size. Common in the United States and

Europe are cone-shaped filters #2, #4, and #6, as well as basket-shaped filters in an 8-12 cup size. Other important parameters are strength, compatibility, efficiency and capacity. (10)

2.4 Migration from Paper

Paper, cardboard and pulp without special coating or other special treatments like coffee filter papers are not suited for a longer contact with wet and/or fatty food materials, migration of substances can occur.
In comparison with plastics low-molecular substances in the polymer matrix are less likely to migrate in the paper matrix. Substances that adsorb on the surface of the paper fibres might play a bigger roll. Also the embedded compounds inside the paper like filler materials play a big factor at migration problems. The division of the substances between the paper and the other atmosphere like coffee always follows a balance which can be influenced by different factors like temperature or time of contact. (4)

Sometimes special factors like the vapour pressure play a big roll, like with **dioxins** which still have a small vapour pressure so they are not very likely to migrate in a normal paper product in contact with food materials. But the coffee brewing applies factors like high temperature which might cause dioxins to migrate even with the short contact time. (4)

Another special group concerning migration are **metals** which are bound as ions inside the paper matrix or as parts of inorganic filler materials. The extraction with water like at coffee brewing offers the biggest chances of a migration of metals. So it is most important that the concentrations are low in the filter papers to begin with. (4)

An experiment determining the metal amount in paper showed for coffee filters: 0,01µg/g, Cd, 0,40µg/g Pb, 0,29µg/g As and 0,01µg/g Hg. Were specially the mercury numbers call for concern. (4)

An additional difference to plastics is the migration of possible contaminations of approved additives. Under the organic components the biggest rolls play **polychlorinated biphenyls** (PCB), **pentachlorophenol** (PCP**), polychlorinated dibenzo-dioxin** (PCDD) and –furans (PCDF). Where in the last years more applications of these substances were forbidden, the safety limits lowered and so the used amounts diminished. But those substances are still present in recycled paper. (4)

2.5 Bleaching of paper – the dioxin problem

A big topic at coffee filter papers is the colour of the product. The colour after pulping depends on the wood species, method of pressing and extraneous components.
Basically, there are two types of bleaching operations: those that chemically modify the chromophoric groups by oxidation or reduction but remove very little lignin or other substances from the papers. And those that complete the delignification process and remove some carbohydrate material. Most modern methods use both the oxidation of coloured bodies and the removal of residual materials (the principal on being lignin). Because bleaching reduces the strength of the pulp, it is necessary to reach a compromise between the brightness of the finished sheet and its tensile proprieties. (5)

Around 1986, the production process for bleached chemical pulp was identified as a major contributor of the **dioxins PCDD** and **PCDF** to the environment. Because these compounds are powerful toxins and carcinogens much investigative activity was carried out in Europe and North America to identify point sources and suggest corrective measures. Chlorine bleaching was identified as the major source of these compounds. (5) (6)
Overall there are 75 possible isomers of PCDDs and 135 of PCDFs and these related compounds are all suspected or to be congeners. Where the most toxic one if 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). (5)

So bleaching of coffee filter papers also was investigated and the migration of the possible harmful substances from the bleaching process:

A carryover rate of about 10% for dioxins from chlorine bleached paperboard cartons into milk and about 28% from coffee filter paper into brewed coffee has been reported. (7)

Nowadays the industry moved away from molecular chlorine bleaching to chlorine dioxide (ECF or elemental chlorine) and to oxygen and peroxide bleaching (TCF or total chlorine free). These changes have been introduced to enable pulp and paper mills to meet tough new antipollution laws and regulations, and to conserve wood, chemicals and energy. (5) (6)
In addition improved washing of unbleached pulp to reduce dioxin precursors prior to the bleaching process reduces the risk. (8)

2.6 Chemical Analytics of paper - substances

The many different paper products result in a variety of many different raw materials and additives which result in a wide field of chemical-analytic methods. So the focus point hast to be set, the other analytical methods concerning the many other important parameters of paper are left out here too. At the analytic of paper in contact with food materials the determination of the following substances has priority: (2)

- Dry matter content of a water extract (2) (3)
- Formaldehyde (2) (3)
- Glyoxal (2) (3)
- Pentachlorophenol (2) (3) (5)
- Other phenol substances (2) (5)

In addition the following substances are often determent:

- Heavy metals (3) (14) (28)
- Melamine (3)
- Nitrosamine (3) (5)
- Polychlorinated Biphenyls (PCB) (3) (5)
- Chloroanisole (5)
- Dioxins (5) (6) (8) (17) (19) (21) (23) (25) (26) (29) (30) (31) (32) (33) (34)
- Fluorochemical paper additives (36)

Sometimes it is also interesting to know of recycled paper was used in the production. Substances indicating recycled papers which are not mentioned above already:

- Trimethyldiphenyldiphenylmethanes (a solvent used in the carbonless copy paper) (20)
- Benzophenone (from the printers ink) (18)

- N-nitrosomorpholine and Morpholine (22)
- Phthalates (24) (34)
- Diisopropylnaphtalene (DIPN) (24) (34) (37)
- Dehydroabietic and abietic acids (27)

2.7 Chemical Analytics of paper – methods

For the different substances there are many different methods to analyse them, specially concerning the migration into foodstuffs:

Inorganic substances - metals:

- First an extraction has to be performed, different solvents can be used. (14) (23) (29)
- The extract can be measured with atomic absorption spectroscopy (15) (16) (17)
- Common anions can be determined by ion selective electrode (17)
- Paper samples can be analysed directly with x-ray fluorescence.

Organic substances:

- Sohxlet or Accelerated Solvent Extraction with different solvents is
- Mostly followed by Gas chromatography – Mass spectrometry (GC-MS)
- Other detectors for GC are possible like thermal energy analyzer (22)
- Photometric tests of substances or products of organic reactions are possible
- Nuclear magnetic resonance (NMR) (20)

2.8 Examples of previous studies

2.8.1 Studies on metals

A study was performed on the **migration of metals from paper** and cardboard with distilled water, 3% acetic acid, 10% ethanol and test-fat. The highest values were obtained with 3% acetic acid and the greatest mobility was found with cadmium in cardboard and mercury in paper. (14)

A radiotracer method was applied to the measurement of inorganic contaminants migrating into food from packaging made from recycled paper and board at a British survey. The only elements detected in the static migration test were zinc and iron, at concentrations close to the detection limit. (28)

2.8.2 Studies on benzophenone

A survey was performed on the migration of **benzophenone from cardboard packages into food**. Benzophenone main source being residue from UV-cured inks and lacquers used to print on the packaging or from the use of recycled paper in the production.
The paper samples were extracted with dichloromethane as a solvent. From 350 samples that used printed carton board packaging 207 (59%) had no significant amount. 143 contained detectable amounts were only 76 (22%) showed really high concentrations from 0,8 to 3,3mg/dm².

71 of the food packed in the positive samples was then analyzed 51 showed detectable benzophenone levels, were only 3 had really high amounts exceeding 5mg/kg. (18)

2.8.3 Studies on dioxins

As said before around 1990 the discussion about bleaching and the dioxin problems resulted in a lot of investigations on this topic also on the paper sector and most studies performed on coffee filter papers analysed the dioxin situation.

A study on **commercially available coffee filter** analysed **semi-volatile organics**, **dibenzofurans** and **dioxins** with **Sohxlet Extraction with dichloromethane** and **GC-MS**. No direct relationship between bleaching method and the presence of halogenated materials in the final filter product was observed. Only in one case was a single dioxin isomer detected. Three semi-volatile species not consistent with natural products were detected in any of the filter papers. Both a chlorine bleached and unbleached paper were found to contained a single brominated species where as tributyl phosphate, a plasticizer for cellulose esters and plastics was found in a single oxygen bleached paper. (17)

The migration of PCDD and PCDF from coffee filter papers was determent in an American study. It was found that a relationship existed between the percent migration and the litres brewed per total weight of filter. Overall, the 2378-TCDF migration rate still appears to be greeter than that observed for 2378-TCDD. (26)

An experimental series analyzing **the ethanol extract with GC-MS** showed the typical distribution of **polychlorinated dibenzo dioxins** (**PCDD) and dibenzofurans (PCDF)** congeners found in most bleached paper products indicated that the source of contamination is the bleaching process. Their experiment showed a significant decree in PCDD/PCDF concentration levels from 1988 to 1991 in **Canadian consumer paper products** for use in personal care or food contact applications. (19)
Other studies looked at the overall situation of PCDD/PCDF levels in consumer paper products in **Canada** (31) or in **Sweden** (32) and their improvements in the late 80's.

A **German survey on the PCDD and PCDF** situation in the local pulp and paper industry also showed a decrease from the 80's to 1992. (25)
In the same year the **German PCDD/PCDF decrease** was also shown in a comparison of cardboard containers, coffee filter papers to recycled paper. (30)

The situation of **Japanese coffee filter papers concerning PCDD and PCDF** was tested in a study. The chlorinated aromatic hydrocarbons 1,2,7,8-TCDF, 2,3,7,8-TCDF and 2,3,7,8-TCDD have been identified as low level contaminations of coffee filter papers on sale to the general public in Japan. With about one third of the total PCDDs and PCDFs contamination being eluted form the filter paper during coffee brewing and almost the same quantity was eluted with hot water. The solvents were analysed by GC-MS. (21)

A German study on the local available **coffee filter papers** showed that about **20-35% of TCDD, TCDF and alklated TCDFs passed from the coffee filter into the coffee extract** in simulated coffee brewing process. The extraction was performed with cyclohexane/ethylacetate and the extract analyzed with GC-MS. (33)

Another German study on **PCDD and PCDF levels in coffee filter paper** found an increase of the reported levels with the polarity of the solvent. Again the different solvents (cyclohexane, dichloromethane/ethanol, acetone/hexane, ethanol, acetone/hexane and acetone) were analyzed with GC-MS. (23)

Since the **extraction** is an important part at the test for dioxins a study looked into the optimization of extraction procedures for the **analysis of TCDD/TCDF** in pulp, paper base stocks and pulp industry solid wastes. Ethanol and ethanol/toluene were found to be the best solvents for pulp and paper. Benzene, benzene/acetone and acid digest were inferior solvents; sadly the most used solvent dichloromethane was not analyzed. (29)

Finally an American study gave an overlook of the **health risks from TCDD/TCDF through consumption of coffee** brewed using bleached pulp-based filters. The conclusion was that comparing the consistently low measured levels of TCDD and/or TCDF in coffee, it can be concluded that the consumption of bleached pulp-based filter-brewed coffee does not present any significant health risk to the coffee consumer. (34)

3 EXPERIMENTAL

The following experiments were always done twice (one repeated test-series) if not state otherwise.

3.1 The samples

The goal of the Diploma work was to give a good overview of the commercial available coffee filter papers in Austria. The samples were bought on the same date in public supermarkets in Vienna. Six different supermarkets were searched for the offered products and seven samples bought. For the best comparison all samples were of the same standardized "size 4".

The sample Nr. 1 from Melitta stands out as the only bleached filter with the typical white colour. The other filters are unbleached and look very similar, only sample Nr. 7 from Lidl shows a very unique paper structure.

3.1.1.1 Melitta Original (bought at Spar)

Only bleached sample – white filter

The Melitta brand is the premium brand under coffee filters. They can be bought in different supermarkets and they offer different kinds from bleached to unbleached, with or without flavour. For the experiments the "Melitta Original" was chosen, with the following details from the packaging or the filter itself:

- Made in Europe
- Nadic Eco Label

3.1.1.2 Spar Kaffeefilter (bought at Spar)

Unbleached light brown filter

The low-cost brand of Spar:

- Made in Europe for Spar
- Unbleached pulp, without glue

3.1.1.3 Hofer Kaffee (bought at Hofer)

Unbleached light brown filter

The low-cost brand of Hofer.

3.1.1.4 Clever Kaffee Filter (bought at Billa)

Unbleached light brown filter

The low-cost brand of Billa:

- Flavour neutral unbleached pulp

3.1.1.5 Brigitta Kaffeefilter (bought at Zielpunkt)

Unbleached light brown filter

The low-cost brand of Zielpunkt:

- Made in Germany
- Flavour neutral quality paper

3.1.1.6 Schlecker AS Kaffeefilter (bought at Schlecker)

Unbleached light brown filter

The low-cost brand of Schlecker:

- Flavour neutral unbleached special paper
- No bonding agent used

3.1.1.7 Aromata Structured Coffee Filter Papers (bought at Lidl)

Unbleached light brown filter (with a unique paper structure)

The low-cost brand of Lidl:

- "Der blaue Engel-Jury Umweltzeichen"

3.2 Determination of the weight and moisture content (Oven drying method)

The experiments followed the instructions of the standard **DIN EN 20287** which are based on the **ISO 287: 1985**. (38)

As a sample one filter of the package was chosen, so in this experiment the mass of one single filter of each brand was also defined.

First the initial mass of the filter was measured on a precision scale.
The filter was then placed in a heating oven at 105°C for 30 minutes. Then it was cooled down in an exsiccator to room temperature and a first measurement was performed to see the loss of weight. These steps were repeated until the dried mass did not change much from one step to another so a repeatable result could be calculated for the moisture content.

The initial mass was varying a bit so the results shown in 4.1 are no average values but the results of one tested filter and its mass-changes after drying. The moisture content was

determent one more time but since the results were pretty much identical these results are not displayed.

3.3 Determination of the contact area of a filter and the area-related mass

The contact area of a single filter is important for a lot of later experiments and gaining results from them. As mentioned in 3.1 all filters are "size 4" filters and so all samples got a nearly identical area. Each filter got two paper sides tucked together without glue just by a force that is connecting the paper fibers on the sides.

Sample Nr. 3, 5 and 6 are a little bit different they got a bulge on one side and a small bay on the other side for a better handling, but this has nearly no influence on the area since they cancel each other out.

All filters were determent to have the same area, which was simply measured with a scaled reference paper.

3.4 Preparation of a cold water extract

The experiments followed the instructions of the standard **DIN EN 645** the German Version **EN 645: 1993** Paper and board intended to come into contact with foodstuffs; Preparation of a cold water extract. (39)

Each sample extract was prepared the same way. At each step latex gloves were used to prevent any contaminations.
First the filters were ripped by hand, no scissors or cutting devise were used. The peaces of 1-2 cm² size were filled in an Erlenmeyer flask (since not enough flasks of the same size were available 250, 500 and 1000ml flasks were used) until 10,0g were reached. There was a little difference in the resulting paper volume - see 4.2.

The flask was then filled with 200ml osmotic water; the paper was always covered well no matter what size the flask had.

At each test-series there were was also a blank sample included, simply a flask without paper and only the osmotic water.

The flasks were then stored for 24 hours in a temperature controlled room at around 23°C.

The liquid extract was then filled into a 250ml volumetric flask, the still wet paper was washed two times with osmotic water and the flask filled up with osmotic water to the 250ml line.

This preparation was done several times for the following experiments, always each of the 7 samples two times with two blanks.

The preparation for the pH-measurements different a little bit from the other tests because here only 2g of paper were used in 150ml Erlenmeyer flasks with only 100ml osmotic water and the extraction only took 1 hour after that the measurements took place.

3.5 Preparation of a hot water extract

The experiments followed the instructions of the standard **DIN EN 647** the German Version **EN 647: 1993** Paper and board intended to come into contact with foodstuffs; Preparation of a hot water extract. (40)

The preparation was the same as described at 3.4 until the 200ml osmotic water was filled in. Now the flasks were put in a water bath under a reflux condenser for 2 hours. The water bath had a temperature of 80°C at start.
It was a little bit difficult to maintain the 80°C at each flask, since up to 6 were stored in one water bath at the same time. Here some fluctuations were noticed from the flasks on the outside of the bath to the ones on the inside where the temperature was a few degrees higher.

After the 2 hours the flasks were left alone to cool down to room temperature on their own and then the filling of the 250ml volumetric flask was done as described in 3.4.

The preparation for the pH-measurements were again just scaled down as in 3.4 mentioned, the heating was only applied for 1 hour.

3.6 Determination of dry matter content

The experiments followed the instructions of the standard **DIN EN 920** the German Version **EN 920:2000** Paper and board intended to come into contact with foodstuffs; Determination of dry matter content in an aqueous extract. (41)

For this experiment the cold water extracts (3.4) and the hot water extracts (3.5) were analysed. Since the extracts had to be evaporated, the extra heating of the hot water extracts before using them was unnecessary.
The extracts were only filtered one time for the first series of the cold water extract. Since there was no optical change in the filtered water (it was already clean) and the out coming result was the same at the repeating test without filtering - this step was disclaimed in all future uses of the cold water extract to prevent any contaminations from the filtering paper.

In all the following experiments the filtering step was also always left out because of the named reasons.

First the exact weight of the evaporating bowls had to be measured. At 105°C the bowls were placed in a heating oven for 30 minutes. After cooling down to room temperate in an exsiccator the first weight was determent. This procedure was repeated until the weight stayed stable.

The bowls were reused and it was interesting to notice that the exact weight could not be matched after one usage, cleaning with hydrochloric acid and the heating oven procedure. But the last step was repeated until mass balance was again reached.

Then potions of the 250ml extract were evaporated in the bowls with a heating plate until all 250ml were gone and only a little drop of brown liquid was left. This last fluid was

evaporated slowly in the heating oven at 105°C. A light-brown dry matter remained notably in the bowls, in the blanks there was nearly nothing of dry matter.

Sometimes the last drop was not evaporated in the oven but happened on the bowl, which resulted in a wrong weight because some of the dry matter was burned and turned a little black. This happened only a few times and is noted at the results.

3.7 Determination of the pH

The experiments followed the instructions of the standard **DIN 53124** the German Version Paper, board and pulp – Determination of pH aqueous extracts. (42)

The extracts were prepared scaled down from the other extracts (3.4, 3.5).

In the instructions it is recommended to test the extracts right after the extraction. This was possible at the coldwater extracts.
At the hotwater extracts again 85°C was applied which might differ a little bit from the recommended slight boiling. But coffee is also prepared with really hot water, so 85°C degrees were chosen.
Since the temperature influences the pH the hotwater extract had to cool down to room temperature which took longer than expected, so sometimes the measurements were done on the next day or at a higher degree, it is recommended not to test the pH over 25°C.

The determination it self was rather simple. A calibrated pH measurement instrument with a thermometer was used. The measurements took place in the temperature controlled room at around 23°C. The result was noted when the pH stayed stable for at least one minute.

3.8 Potassium permanganate method

3.8.1 Concept of the determination

The experiments followed the instruction „**Titration der wässrigen Extrakte mit Kaliumpermanganat-Lösung**“. This instruction is based on experiments with plastics, but it could be converted to the analyses of the paper filters. (43)

Potassium permanganate oxidises organic substances in the extract. It is just an empiric method since the error can be rather high because organic substances which are not soluble with water might not be oxidised and the amount of oxidised substances might not be proportional.

3.8.2 Reagents

- Potassium permanganate solution (0,001n)
- Oxalic acid (0,001n)
- Acid sulphur

3.8.3 Experimental procedure

In the instructions tap water is mentioned for the method, but for a better comparison osmotic water was used at this test as well.

200ml of the coldwater extract were evaporated in a rotary evaporator. To the remains 200ml osmotic water were given. The flask with the distillate was directly analysed.

Both flasks were tested for organic substances with the following titration.

To the solution 2,5ml of a 1:4 acid sulphur / osmotic water solutions were given. This mixture was heated until boiling. Now 10ml potassium permanganate solution (0,001n) portions were given until the violet colour was permanent.

Now the last 10ml portion which was not used in the organic reaction was determent with titration with the use of oxalic acid (0,001n). Then the solution turned colourless again which some difficulties (see 4.5).

3.9 Determination of glyoxal content

3.9.1 Concept of the determination

The experiments followed the instructions of the standard **DIN 54603** the German Version Testing of paper, paperboard and board – Determination of glyoxal content. (44)

The determination is based on an organic reaction of the solved glyoxal with 2-Hydrazono-2,3-dihydro-3-methylbenzothialzole-hydrochloride (HMBT) in an acetic solution:

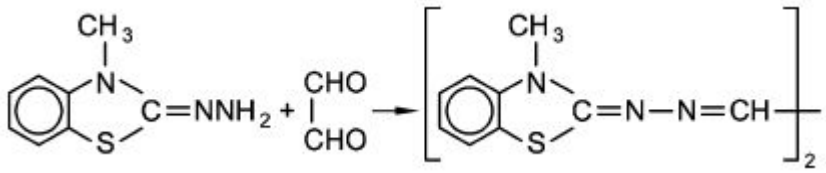

Figure 1: glyoxal content

The reaction product got a yellow colour and the amount can be measured with a photometer at 405nm. The reaction product with the similar formaldehyde is colour less and does not influence the result of the glyoxal content.

3.9.2 Reagents

- Ethanol
- Acetic acid (96%)
- Glyoxal (~30% solution in water)
- HMBT 2-Hydrazono-2,3-dihydro-3-methylbenzothialzole-hydrochloride
- Hydroxylammonium chloride (1 mol/l)
- Methylene blue
- Methylene red
- Sodium hydroxide solution (1 mol/l)

3.9.3 Instruments

Photometer

3.9.4 Experimental procedure

3.9.4.1 Establishment of the reference curve

For the final determination of the glyoxal content in the extracts a reference curve had to be established.

First the exact glyoxal content in the standard reagent had to be determent, because it is labelled as a solution in water of about 30%. For this ~1g of the glyoxal solution, 20ml of Hydroxylammonium chloride, 50ml osmotic water were mixed.
After 30 minutes this solution was titrated with the indicator of Toshiro (a mix of methylene blue and methylene red in ethanol) against the sodium hydroxide solution. This was repeated 3 times for a good average value.

When the exact content was known, the **first standard solution** could be made: In a 100ml volumetric flask an equivalent of 100mg glyoxal was weigh in and filled up to the mark with osmotic water.
From this first standard solution 1ml was filled up again to 100ml in a second volumetric flask to gain a concentration of 1mg glyoxal for the **second standard solution**.

Out of the second standard solution the four solutions for the reference curve could be made:
First the **HMBT-solution** had to be prepared, for this 0,4g of the solid reagent was dissolved in a solution of 1:1 water and acetic acid (96%).
Then 0,5ml (5 µg glyoxal), 1,0ml (10 µg), 2,0ml (20 µg) and 3,0 (30 µg) of the second glyoxal standard were put in a 25ml volumetric flask. Then 2,5ml of the HMBT-solution is mixed in. With a 1:1 water to acetic acid (96%) solution the volumetric flask was filled up to the 25ml mark.
These solutions were put into a water bath of 80°C for 5 minutes. After that they were cooled down to room temperature with the help of running water.

Now a portion of the solution could be tested at 405nm at the photometer against the blanks which was prepared the same way except only osmotic water was used for the first standard solution.
With the results the reference curve can be established with the concentration against the absorption. The resulting curve was very linear so this was not repeated.

When the sample extracts were tested the absorption results of those were lower than the 5µg glyoxal point, so two lower concentrations of 0,5, 1 and 2µg solutions were made. The resulting absorptions were also in the linear area of the curve but were not included in the later calculations because the instructions mentioned results under the last recommended point of 5µg are not that reliable.

3.9.4.2 Determination of the glyoxal content in the extracts

10ml of the coldwater or hotwater extracts were mixed with 10ml acetic acid (96%) and 2,5ml HMBT-solution in a 25ml volumetric flask. Again with a 1:1 water to acetic acid (96%) solution the volumetric flask was filled up to the 25ml mark.
The heating (5min at 80°C) and cooling steps of the standard solution were also applied. Then the photometric measurement against a blank-solution was done under the same settings as the standard solutions.

3.9.4.3 Control test of the glyoxal content

Since the absorbance outcomes of the sample extracts were pretty low and close to the blanks, the question came up if the data shows reproducible concentrations or if it just represents the error of the photometer within the detection limit.

So an additional test was performed. Sample Nr. 6 showed the highest absorbance, so another cold water extract was made with only sample Nr. 6. But this time 10g filter paper was extracted with only 100ml osmotic water. The photometer should represent the double absorbance since the same amount of paper is extracted with only half the volume of liquid. In the end the resulting concentration should be the same, again two separate extracts were prepared.

3.10 Determination of formaldehyde content

3.10.1 Concept of the determination

The experiments followed the instructions of the standard **DIN EN 1541** the German Version **EN 1541:2001** Paper and board intended to come into contact with foodstuffs – Determination of formaldehyde in aqueous extract. (45)

The determination is based on an organic reaction of the solved formaldehyde with acetyl acetone to 3,5-diacetyl-1,4-dihydrolutidin.

The reaction product got a yellow colour and the amount can be measured with a photometer at 410nm.

3.10.2 Reagents

- Drained ammonium acetate
- Acetic acid (99%)
- Acetyl acetone (Penta-2,4-dion)
- Hydrochloric acid (1 mol/l)
- Sodium hydroxide solution (1 mol/l)
- Starch solution (2 g/l)
- Formaldehyde-solution (370 to 400 g/l)
- Standard-iodine-solution (0,05 mol/l)
- Standard- sodium-thiosulfate-solution(0,1 mol/l)

3.10.3 Instruments

Photometer

3.10.4 Experimental procedure

3.10.4.1 Establishment of the reference curve

First a reagent called Penta-2,4-dion reagent in the instructions had to be prepared:
In a 100ml volumetric flask 15,0g drained ammonium acetate were dissolved in 0,2ml acetyl acetone, 0,3ml acetic acid, the flask was filled up to the 100ml mark with osmotic water.

Now the exact concentration of the formaldehyde-standard-solution had to be determent.
From the formaldehyde-solution (370 to 400 g/l) 5ml were filled in a 1000ml volumetric flask. The flask was filled up to the 1000ml mark with osmotic water.

10ml of this solution were mixed with 25ml standard-iodine-solution (0,05 mol/l) and 10ml sodium hydroxide solution (1 mol/l) in an Erlenmeyer flask.
After 5 minutes 11,0ml hydrochloric acid (1 mol/l) and a small portion of the starch solution (2 g/l) was added. The hydrochloric acid makes the solution acidic and the starch solution serves as an indicator for the titration.
Now the concentration can be determent with a titration of the unused iodine against the standard- sodium-thiosulfate -solution.

Now the concentration was known and the reference curve could be established with this formaldehyde-standard-solution:
Six concentrations were measured: 1ml, 5ml, 10ml, 15ml, 20ml or 35ml of the 1000ml formaldehyde-solution were mixed with 5ml of the Penta-2,4-dion reagent and 24ml osmotic water in a 50ml Erlenmeyer flask.

The Erlenmeyer flask was put into a water bath at 60°C for 10 minutes. After cooling the solution down to room temperature the extinction could be measured at 410nm against a blank at the photometer.

With these 6 points the reference curve was established. Since the curve was pretty linear and the points within the later results of sample concentrations, no additional points were added.

3.10.4.2 Determination of the formaldehyde content in the extracts

25ml of the cold or hotwater extract were mixed with 5ml Penta-2,4-dion reagent in a 50ml Erlenmeyer flask.
Now the same conditions were applied as at the reference solutions - water batch at 60°C for 10 minutes and measurement after cooling down at 410nm at the photometer against a blank.

3.11 Determination of pentachlorophenol content

3.11.1 Concept of the determination

Since no DIN method for the photometric measurement of pentachlorophenol exists because this method is outdated, the experiments followed the instructions of book which contains methods for the chemical analysis of paper and pulp. (46)

Pentachlorophenol reacts with 4-Amino-Antipyrin (4-Amino-2,3-dimethyle-1-phenyle-3-pyrazolin-5-on) to a green reaction product when a weak oxidant is present like potassiumhexacyanoferrat(III).

This green reaction product can be measured in benzene at 585nm at a photometer

3.11.2 Reagents

- Hydrochloric acid
- Ether
- Ethanol caustic potash
- Borax
- Monopotassiumphosphate
- Benzene
- Potassiumhexacyanoferrat(III)
- 4-Amino-Antipyrin

3.11.3 Instruments

Photometer

3.11.4 Experimental procedure

3.11.4.1 Determination of the pentachlorophenol content in the extracts

All 7 samples and a blank were tested; again a repeated test-series was performed too. To see if the experiment even worked only two series of fresh prepared coldwater extracts were analyzed. The instructions also only speak of a method for a coldwater extract.

The 250ml extract in the volumetric flask were acidulated with a few drops of concentrated hydrochloric acid. The whole extract was put in a separating funnel with ether to perform a solvent extraction. Since no definite amount of ether was given in the instructions, 150ml were used.

The ether-phase was used onwards. A few drops of an ethanol caustic potash were added and the ether evaporated in a rotary evaporator. To the residue 50ml of a buffer-solution, this volume was again not given by the instructions.

This buffer-solution was mixed based on the instructions in the book:
14,15g borax ($Na_2B_4O_7 * 10\ H_2O$) and 8,17g Monopotassiumphosphate (KH_2PO_4) is dissolved in a 100ml volumetric flask with osmotic water which is filled in until the 100ml mark was reached.
This method was used it only got scaled up to a 1000ml volumetric flask.

The 50ml were filled in a separating funnel and another solvent extraction was performed with 50ml benzene, 5ml Potassiumhexacyanoferrat(III)-solution and 5ml of a 4-Amino-Antipyrin solution. Again those volumes were not given in detail by the instructions.

The preparation of the Potassiumhexacyanoferrat(III)-solution was given by the instructions: 6,0g Potassiumhexacyanoferrat(III) was dissolved in 100ml osmotic water. Again this reagent was scaled up to a 1000ml volume.

A part of the benzene-phase which was yellow coloured was measured at 585nm at the photometer against a blank.

3.11.4.2 Establishment of the reference curve

A **reference curve** was also tried to establish with the photometer, sadly no instructions were given on how to proceed here, so this was done after the samples had been analysed:
Since no method for the determination of the concentration of the standard was available either and the concentration was given with a precise number of 100µg/µl, this labelling information was trusted.

First the amount to get to a 0,005; 0,01; 0,02 and 0,04µg/µl concentration after diluting up to 2ml was calculated. To that amount 0,2ml Potassiumhexacyanoferrat(III)-solution and 0,2ml 4-Amino-Antipyrin was given.
This mixture was filled up to 2ml with methanol, since the standard pentachlorophenol-solution was based on methanol.
Sadly this liquid turned into a foggy orange solution which could not really be measured at the photometer.

So the method was tried again but this time it was filled up to 2ml with benzene. This solution was yellow as the samples and could be tested at the photometer against a blank.

3.12 Scanning Electron Microscope

Only two filter samples could be tested simultaneously with the Scanning Electron Microscope and because the results were acceptable no additional samples were scanned.

Sample Nr. 1 and 4 were used to see if there is a difference between bleached (1) and unbleached (4) filter paper.

A small peace of about 1cm² was cut out of both filters and put on the sample container. The bleached white filter was marked with a W.

Then the sample container was put into the vaporising chamber and the samples were vaporised with platinum.

After some time the samples could be observed and images at different settings were taken.

3.13 Headspace Gas Chromatography – Mass Spectrometry

3.13.1 Concept of the method

A sample is put in a 150ml vial without any additional preparation. The vial is plugged with a gas proof cap. According to the installed settings the vial-cap is pierced with the gas chromatography needle at a certain temperature for a certain time and a pressure is applied. After that a portion of the gas-volume of the vial is put through the gas chromatograph and analysed wit a mass spectrometer.

3.13.2 Reagents

No reagents are necessary for the measurements. But for the certification of some signals the following standards were used:

- 1-Heptanol
- 1-Octanol
- 1-Nonanol
- Benzaldehyde
- Acetophenone

3.13.3 Instrument and measurement settings

A **Headspace Turbo Mass PerkinElmer** was used with the following settings at all measurements:

Temperature settings:

- Needle: 210°C
- Transfer Line: 210°C
- Vial Oven: 150°C

Time settings:

- Inject: 0,04min
- Pressure: 3.0min
- Withdraw: 0,1min
- Thermostat: 60min
- GC Cycle: 70min

Pressure settings:

- 100kPa (1bar)

3.13.4 Experimental procedure

3.13.4.1 Analyses of the untreated filter papers

For a good comparison always 1dm² was cut out of the each filter. Again two test-series were performed. The peaces were filled in the 150ml vial and the vial was plugged with a gas proof cap. One vial was left empty as a blank.
Then the settings for the analyses were installed and the measurements started.

3.13.4.2 Analyses of the extracted filter papers

To compare if the Accelerated Solvent Extraction (ASE) extracted any substances which are shown in the results of the headspace test of the untreated paper, another two test-series were performed.
Here the same method as above was used with the paper leftover materials of the Accelerated Solvent Extraction for the Multimethod (3.15.1).

3.13.4.3 Additional measurements

Because the question of migrating substances from the package was still present, ~2g of the packages of sample Nr. 1, 2 and 3 were tested twice again under the same settings.

Some of the package-chromatograms in combination with the spectre analyses of certain peaks suggested some substances. To confirm some additional vials with standards were prepared. In one vial 1µl, in the next two 2µl of each standard mentioned in 3.13.2 were filled in. The same settings were used to get a chromatogram of the standards. This chromatogram could then be compared to the original ones of the packages.

In addition some other cardboard samples were tested, bleached and unbleached from packages or filler material. Since those samples were just for comparison and did not give any interesting results, they are not included in the result section.

3.14 X-ray fluorescence spectroscopy

3.14.1 Concept of the method

The samples were analysed with an X-ray fluorescence spectroscope to get their elemental composition from sodium. Lighter elements are not shown and also the light elements like sodium or magnesium are not that reliable.

3.14.2 Instrument and measurement settings

An energy dispersive X-ray spectroscope named **Spectro X-Lab2000** was used. The measurements were done without a calibration with external standards.
Three different targets were used for the measurements. A preset method for paper products was used with the following settings:

Table 1: Method settings fort he X-ray spectroscopy

Target	molybdenum	corundum	highly oriented pyrolytic graphite
Voltage [kV]	39,9	49,4	15
Current [mA]	5,5	6	12,9
Measuring time [s]	150	150	150
Impulse rate [cps]	19000	1000	2000
Down time [%]	32	2,5	6,5
Peak time [µs]	30	30	55

Energy field [keV]	25	50	12,5
Zero-peak-rate [cps]	5000	5000	5000

Some settings like the current fluctuated a little bit from the given one during the measurements but overall they stayed in range to get the same conditions for all samples.

3.14.3 Experimental procedure

Six filter papers were put on top of each other and a 32mm diameter square was cut out of all layers (this diameter filled the whole cell). This resulted in a paper mass of about 1g. This matter was put into one slot of the spectroscope. Like always the filter papers were chosen at random from the package, not knowing if they had been on the outside in contact with the inner layer of the cardboard of the package.
So all chambers of the spectroscope were filled with 1g of paper filter samples, again two test-series of all seven samples were performed.

To get an indication if some metals migrated from the packaging to the filter papers, they were analysed too. Here a small portion of the package of about 1g was cut out and again put into one chamber of the spectrometer. Here only one series of all seven packages was performed.

After filling all chambers the measurements could be started with the settings described in 3.14.2.

3.15 Gas Chromatography Multimethod – Mass Spectrometry

3.15.1 Concept of the method

The method followed the instructions of a multimethod developed at the “Fraunhofer Institut – Verpackungstechnik und Verpackung”.

This method is a combination of different experimental determination of certain substances simultaneously from one extract.
The extraction was done by Accelerated Solvent Extraction the recommended extracting agent dichloromethane was used.

The resulting extract was then analysed directly or after some preparation steps with Gas Chromatography – Mass Spectrometry.

Some substances included in the Multimethod were not analysed because of various reasons like the lack of a proper standard but the most interesting chemicals were analysed.

3.15.2 Reagents

Cleaning agents:

- n-hexane
- acetone

- Mucasol©

Extracting agent:
- Dichloromethane

Standard substances (for each sample):
- 4µl D4-Dibutylphtalat(DBP) (98%) 1439µg/ml in toluol
- 8µl D4-Diethylhexylphtalat(DEHP) (98%) 769ppm in toluol
- 5µl 13C Pentachlorophenol (PCP)
- 50µl Polychlorinated biphenyl (PCB) 100ppm

Reagents for the determination of pentachlorophenol:
- potassium carbonate (0,1M)
- n-hexane
- acetic anhydride

3.15.3 Instrument and measurement settings

Settings for the **pre-extraction** of the empty cartridges with Accelerated Solvent Extraction
- Extracting agent: dichloromethane
- Static phase: 5
- Temperature: 80°C
- Pressure: 100bar
- Volume 20ml
- 3 cycle
- Flush 60%
- Purge 200sec

Settings for the **extraction** of the sample-filled cartridges with Accelerated Solvent Extraction
- Extracting agent: dichloromethane
- Static phase: 15
- Temperature: 80°C
- Pressure: 100bar
- Volume 20ml
- 3 cycle
- Flush 60%
- Purge 200sec

The gas chromatograph **Shimadzu QP-5000 MS** was used with the following settings:
- Column DB-5MS:
  - Length: 60m
  - Internal diameter: 0,25mm
  - Film: 0,25µm
- Temperature program:
  - 80°C 2min
  - 15°C/min -> 100°C
  - 5°C/min -> 215°C
  - 20°C/min -> 300°C

- 3min

3.15.4 Experimental procedure

3.15.4.1 Sample Preparation Accelerated Solvent Extraction

First the cartridges for the Accelerated Solvent Extraction (ASE) had to be prepared. They were taken apart and the peaces were cleaned on time with n-hexane and acetone and one time with a Mucasol© aqua bi-distilled water solution in an ultrasonic bath. After that they were dried in a heating oven at 100°C for half an hour.

Then the peaces were put together again and the pre-extraction of the empty cartridges was performed. Here the pre-extraction method was used. This was just an additional cleaning step, every contamination that might be left after the cleaning with the different solvents, was now extracted with dichloromethane.

Then the cleaned empty cartridges were filled with the sample material. 1dm² was cut out of each sample and the exact weight was determent. Then this 1dm² was cut into small peaces with a metal pair of scissors, between each sample it was cleaned with acetone.

Again 14 cartridges were filled for a repeated test-series, two cartridges stayed empty as blanks. Then the standard substances were filled onto the samples with a micro needle (3.15.2).

Those standard substances were later used to determent the concentrations of all the substances compared to the extraction results of those known internal standards. The calibration with those standards was already established and was not performed again at the experiments.

Then the cartridges were closed and put into the ASE chambers. The 25ml vials, where the resulting extracted is stored, were cleaned with n-hexane and acetone too. They were also put into the right chambers.

Then the settings of the extraction were loaded and started.

3.15.4.2 Determination of Phthalates

1ml of the extracts (total ~20ml) were taken and filled into gas chromatography vials. Until this step no gloves were used and all reagents were stored in containers not based on plastic since contaminations of phthalates from different sources are very easy to obtain.
The vials were capped with an aluminium foil to prevent any contaminations from the plastic of the cap.
Now the 14 sample vials and the two blanks could be measured with the gas chromatography – mass spectrometry.

3.15.4.3 Determination of Pentachlorophenol

10ml of the extracts were taken and put into screw cap vials. For this analysis with the gas chromatography a derivatisation step had to be performed.
A 0,1M potassium carbonate solution with bi-distilled water was prepared. The 10ml extracted were shaken out with 2ml of the solution for 10 minutes. The aqueous ~2ml phase was drawn off and stored in another screw cap vial. Then the shaking step was repeated 2 more times with the organic phase.

In the end ~6ml aqueous potassium carbonate phase was collected. To those 2ml n-hexane and 0,3ml acetic anhydride were given. This solution was shaken for 7 minutes. Then another 0,1ml acetic anhydride was filled in and the solution was shaken for another 3 minutes. The acetic anhydride is the derivatisation agent for the pentachlorophenol.

The n-hexanephase (~2ml) was drawn off and 50µl Polychlorinated biphenyl (PCB) standard were given. So the extract could also be quantificated for these substances.

As a last cleaning step the n-hexanephase was filled onto ~3ml of bi-distilled water and the solution was shaken slightly. Then a part of the organic n-hexanephase was filled in a 1ml gas chromatography vial. Now those vials could be analysed for mainly pentachlorophenol with the internal standard but because of the similarity it was also possible to determent the amount of all other substituted chlorophenols.

3.15.4.4 Determination of Benzophenone

3.15.4.5 Determination of Diisopropylnaphthalene

3.15.4.6 Determination of Michler's ketone

3.16 Determination of Dioxins

3.17 Determination of perfluorinated compounds

3.18 Gas Chromatography Echelle Plasma Emissions Detector

3.18.1 Concept of the method

The **Echelle Plasma Emissions Detector** (EPED) is a special detector for gas chromatographs for sulphur and halogens (chlorine, bromine, fluorine and iodine). The molecules of the sample are atomized at 8000K and atmospheric pressure in a helium plasma.

The detection of emission lines is then done with a polychromator. The biggest advantage is the very low detection limit (< 10 pg/s) for the mentioned elements.
At the used gas chromatograph a **purge and trap** system was used for the sampling of the chromatograph to enhance the results even further.

3.18.2 Experimental procedure

0,25dm² were cut out of each sample paper, filled into 150ml vials, and then the vials were capped. Then no other preparation was necessary, the vials were automatically measured with an auto-sampler at the GC-EPED instrument for fluorinated substances. The main target were **perfluorinated compounds** and with special standards the amount of **fluorotelomer alcohol** (FTOH) and **fluorotelomerthiol** (FTSH) could be determent.

4 RESULTS AND DISCUSSION

4.1 Results of the determination of the weight and moisture content (Oven drying method)

Table 2: Initial, dried mass of each filter brand and the resulting moisture content

Sample	Initial mass [g]	Dried mass [g]	Moisture content [%]
1	1,84	1,82	1,0
2	1,80	1,78	1,1
3	1,74	1,71	1,2
4	1,76	1,74	1,2
5	1,63	1,62	0,6
6	1,65	1,65	0,2
7	1,80	1,81	0,0

The numbers show that the determination was not as precise as hoped. The moisture content seems to be so low that many other factors are influencing the result like air humidity or the high room temperature during the summer when the determination was performed. The dried mass was not stable, even when waited a long time in the exsiccator, so only two decimals are shown and even these were varying a little bit.

The most surprising result was found at filter Nr. 7 because the mass was not changing much at all.

But overall the experiment showed that the moisture content of the coffee filter papers is low for paper. This is also important for other determinations since the moisture content plays and part there. So it is welcomed that it does not play a big roll in the mass and there is not much difference between the filters themselves.

4.2 Results of the determination of the contact area of a filter and the area-related mass

The contact area was determent with 1,4375 dm² for one side or 2,875 dm² for the howl filter. In the following chart the weight from 4.1 and the contact area are combined to show important numbers for the following experiments:

Table 3: The contact area and the area-related mass

Sample	1 filter [g]	10g correspond to individual filters	10g correspond to [dm²}	Area-related mass [g/m²]
1	1,84	5,43	15,63	64,0000
2	1,80	5,57	16,00	62,5009
3	1,74	5,76	16,56	60,3930
4	1,76	5,68	16,32	61,2626
5	1,63	6,12	17,59	56,8452
6	1,65	6,06	17,41	57,4330
7	1,80	5,54	15,94	62,7374

4.3 Results of the determination of dry matter content

4.3.1 Experimental results

In the following tablets the results of the 4 measurement series are shown:

Table 4: Coldwater extract 1. measurement

Sample	Weight of the bowl [g]	Weight after evaporating [g]	Dry matter [g]
1	81,0515	81,0747	0,0232
2	79,6088	79,6201	0,0113
3	43,3474	43,3499	0,0025
4	19,9568	19,9592	0,0024
5	81,0568	81,0656	0,0088
6	79,6105	79,6206	0,0101
7	43,3471	43,3576	0,0105
B	80,8835	80,8854	0,0019

Table 5: Coldwater extract 2. measurement

Sample	Weight of the bowl [g]	Weight after evaporating [g]	Dry matter [g]
1	81,0556	81,0746	0,0190
2	79,6108	79,6203	0,0095
3	43,3478	43,3533	0,0055
4	80,8836	80,8907	0,0071
5	81,0555	81,0614	0,0059
6	79,6109	79,6187	0,0078
7	43,3480	43,3552	0,0072
B	80,8838	80,8842	0,0004

Table 6: Hotwater extract 1. measurement

Sample	Weight of the bowl [g]	Weight after evaporating [g]	Dry matter [g]
1	81,0563	81,0654	0,0091
2	79,6108	79,6201	0,0093
3	43,3478	43,3513	0,0035
4	80,8849	80,8891	0,0042
5	81,0564	81,0634	0,0070
6	79,6109	79,6198	0,0089
7	43,3480	43,3575	0,0095
B	80,8835	80,8844	0,0009

Table 7: Hotwater extract 2. measurement

Sample	Weight of the bowl [g]	Weight after evaporating [g]	Dry matter [g]
1	81,0563	81,0699	0,0136
2	79,6108	79,6201	0,0093
3	43,3478	43,3553	0,0075
4	80,8849	80,8885	0,0036
5	81,0564	81,0673	0,0109
6	79,6109	79,6226	0,0117
7	43,3480	43,3590	0,0110
B	80,8835	80,8841	0,0006

B stands for the blanks. The red test results are marked because here the last drop was not evaporated in the heating oven but on the bowl, so the result is not accurate and should be cancelled out.

The instructions recommend that at least 5mg should be the result to be representative or more liquid should be used. The results show that this goal was mostly reached; only the blanks which contain only osmotic water are understandable much lower.

The result of the first coldwater extract measurement might be a little bit higher since a filtering step was included here; the numbers of the blanks also suggest this.

4.3.2 Calculation of the dry matter content

The calculation followed the formula from the DIN instruction:

$$M = (m_a - m_b) \times \frac{V_o}{V_1} \times \frac{1000}{m} \times \frac{100}{(100 - f)}$$

Formula 1: Determination of the water soluble dry matter content in mg/kg

M…the water soluble dry matter content [mg/kg]
m_a…the evaporating residue of the extract after the Evaporating [mg]
m_b…the evaporating residue of the used osmotic water [mg]
V_0…the volume of the extracts (250ml) [ml]
V_1…the volume of the evaporated part of the extracts (mostly everything 250ml) [ml]
m…the weight of the sample at preparation of the extract (10g) [g]
f…the moisture content of the sample (4.1) [%]

The calculated data is shown in the next tablets:

Table 8: Results of the 1. coldwater extract (K1)

Sample	m_a [mg]	m_b [mg]	V_0 [mg]	V_1 [mg]	m [g]	f [%]	M [mg/kg]
1	23,2	1,9	250	100	10,0	1,0	5381
2	11,3	1,9	250	100	10,0	1,1	2376
3	2,5	1,9	250	100	10,0	1,2	152
4	2,4	1,9	250	100	10,0	1,2	126
5	8,8	1,9	250	100	10,0	0,6	1736
6	10,1	1,9	250	100	10,0	0,2	2054
7	10,5	1,9	250	100	10,0	0,0	2150

Table 9: Results of the 2. coldwater extract (K1)

Sample	m_a [mg]	m_b [mg]	V_0 [mg]	V_1 [mg]	m [g]	f [%]	M [mg/kg]
1	19,0	0,4	250	100	10,0	1,0	4699
2	9,5	0,4	250	100	10,0	1,1	2300
3	5,5	0,4	250	100	10,0	1,2	1291
4	7,1	0,4	250	100	10,0	1,2	1695
5	5,9	0,4	250	100	10,0	0,6	1384
6	7,8	0,4	250	100	10,0	0,2	1854
7	7,2	0,4	250	100	10,0	0,0	1700

Table 10: Results of the first hotwater extract (H1)

Sample	m_a [mg]	m_b [mg]	V_0 [mg]	V_1 [mg]	m [g]	f [%]	M [mg/kg]
1	9,1	0,9	250	100	10,0	1,0	2071
2	9,3	0,9	250	100	10,0	1,1	2123
3	3,5	0,9	250	100	10,0	1,2	658

4	4,2	0,9	250	100	10,0	1,2	835
5	7,0	0,9	250	100	10,0	0,6	1535
6	8,9	0,9	250	100	10,0	0,2	2004
7	9,5	0,9	250	100	10,0	0,0	2150

Table 11: Results of the second hotwater extract (H2)

Sample	m_a [mg]	m_b [mg]	V_0 [mg]	V_1 [mg]	m [g]	f [%]	M [mg/kg]
1	13,6	0,6	250	100	10,0	1,0	3284
2	9,3	0,6	250	100	10,0	1,1	2199
3	7,5	0,6	250	100	10,0	1,2	1747
4	3,6	0,6	250	100	10,0	1,2	759
5	10,9	0,6	250	100	10,0	0,6	2591
6	11,7	0,6	250	100	10,0	0,2	2781
7	11,0	0,6	250	100	10,0	0,0	2600

Table 12: Summary and average values (av.) of the water soluble dry matter content

Sample	M K1 [mg/kg]	M K2 [mg/kg]	av. K [mg/kg]	M H1 [mg/kg]	M H2 [mg/kg]	av. H [mg/kg]
1	5381	4699	5040	2071	3284	2678
2	2376	2300	2338	2123	2199	2161
3	152	1291	722	658	1747	1203
4	126	1695	911	835	759	797
5	1736	1384	1560	1535	2591	2063
6	2054	1854	1954	2004	2781	2393
7	2150	1700	1925	2150	2600	2375

It is also possible to calculate the dry matter content with different formula to get a result in [mg/dm²]:

$$M = (m_a - m_b) \times \frac{V_o}{V_1} \times \frac{b}{100} \times \frac{1}{m}$$

Formula 2: Determination of the water soluble dry matter content in mg/dm²

b…the initial mass of a filter (4.1)

The following tablet illustrates the results:

Table 13: The soluble dry matter content in [mg/dm²]

Sample	M K1 [mg/dm²]	M K2 [mg/dm²]	av. K [mg/dm²]	M H1 [mg/dm²]	M H2 [mg/dm²]	av. H [mg/dm²]
1	0,00068	0,00060	0,00064	0,00026	0,00042	0,00034
2	0,00029	0,00028	0,00029	0,00026	0,00027	0,00027
3	0,00002	0,00015	0,00009	0,00008	0,00021	0,00014
4	0,00002	0,00021	0,00011	0,00010	0,00009	0,00010
5	0,00020	0,00016	0,00018	0,00017	0,00029	0,00023
6	0,00024	0,00021	0,00022	0,00023	0,00032	0,00027
7	0,00027	0,00021	0,00024	0,00027	0,00033	0,00030

4.3.3 Discussion of the results

Sources of error could be the exact weight of the bowls; maybe an error of +/- 1mg can be included here.

The same error could occur when the final weight of the bowls with the dry matter was determent.

Another source might come from the used pipettes since handling with a little bigger volume of 250ml, 50ml pipettes were used, but the error should be really low since the howl 250ml were transferred from the flask to the bowl in multiple steps.

The biggest error can be found at the heating plates. The bowls were not exactly the same shape and the plates heated not exactly in the same intensity. So the evaporation-time differed a little bit, this might had an influence on the end result.

The heating should be done slowly to make sure that no drops are spilled out. This was tried as best with the available heating plates which could not be regulated to the point that a good heating was applied and no heavy boiling occurred. So some small errors may have happened to spilling drops at the evaporating.

All these errors can also be seen at the fluctuating results of the blanks, but since these fluctuations are also tolerable the overall error of the experiment seems to be within the guidelines of the DIN instruction.

At the calculation the error that might have occurred at the determination of the moisture content played a factor but this error seems to be low too.

But this pre-test went relatively well and so some **conclusions** can be drawn:

- The bleached filter Nr. 1 always has the biggest dry matter content
- The other six unbleached filters provide similar results, only the filter Nr. 4 differs a little bit but in the end the dry matter content seems to be in the same range for all unbleached samples
- The hotwater extraction should result in higher dry matter content from experience, the results back this up to some degree but a total conclusion in this direction could sadly not drawn
- The colour of hotwater extract was light-brown/yellow and the coldwater extract turned to this colour as well during the heating, also the bleached filter showed the same colour as all the other samples. The blanks remained colourless.

4.4 Results of the determination of the pH

4.4.1 Experimental results

In the following tablets the results of the pH readings are listed, the shown numbers are average values of two following series:

Table 14: Coldwater extract 1. measurement

Sample	pH	at T [°C]
1	7,23	24,6
2	7,23	24,9
3	7,24	25,2
4	7,51	25,4
5	7,53	25,5
6	7,31	25,8

7	7,18	26,5
B	6,85	26,3

This first measurement was not done in the temperature controlled room, so the temperature is higher und not as stable. In conclusion to this the other series were tested in this room at a stable temperature as mentioned in 3.7.

Table 15: Coldwater extract 2. measurement

Sample	pH	at T [°C]
1	7,18	24,4
2	7,00	24,1
3	7,15	24,0
4	7,44	23,9
5	7,26	23,7
6	7,29	23,2
7	7,05	23,2
B	6,47	22,9

The results show that the temperature might not been as stable as recommended since it dropped from sample 1 to 7.

Table 16: Hotwater extract 1. measurement

Sample	pH	at T [°C]
1	6,94	21,1
2	7,08	21,0
3	7,13	21,0
4	7,09	21,0
5	7,07	20,9
6	7,07	20,9
7	7,06	21,0
B	6,63	21,0

This test was done on the following day of the extraction because a stable temperature could not be reached on the day before, now the temperature was really stable

Table 17: Hotwater extract 2. measurement

Sample	pH	at T [°C]
1	7,24	23,0
2	7,16	23,0
3	7,31	23,1
4	7,41	23,2
5	7,20	23,0
6	7,19	22,9
7	7,10	23,1
B	6,76	23,1

This series was done again on the following day of the extraction. Sadly the temperature of the controlled room was also 2 degrees higher than on the other test day.

Table 18: pH Summary

Sample	pH K1	at T [°C]	pH K2	at T [°C]	pH H1	at T [°C]	pH H2	at T [°C]
1	7,23	24,6	7,18	24,4	6,94	21,1	7,24	23,0
2	7,23	24,9	7,00	24,1	7,08	21,0	7,16	23,0
3	7,24	25,2	7,15	24,0	7,13	21,0	7,31	23,1
4	7,51	25,4	7,44	23,9	7,09	21,0	7,41	23,2

5	7,53	25,5	7,26	23,7	7,07	20,9	7,20	23,0
6	7,31	25,8	7,29	23,2	7,07	20,9	7,19	22,9
7	7,18	26,5	7,05	23,2	7,06	21,0	7,10	23,1
B	6,85	26,3	6,47	22,9	6,63	21,0	6,76	23,1

4.4.2 Discussion of the results

One **source of an error** the temperature was mentioned in greater detail already. All samples should have been tested at a stable temperature under 25°C within an hour of the extraction. This was impossible to accomplish because of different reasons.
Either to reach the stable temperature (even in the controlled room) took too long or it simply was not as stable as recommended.

Another error could occur from the used pH meter. Normally it should present a stable pH after some seconds. But sometimes the pH was rising or falling for minutes. So the results were always noted after the pH stayed stable for around a minute, often after waiting 5 or more minutes.

Nevertheless the errors might influence the second decimal place and overall the numbers do not differ that much from each other. The instructions also tolerated a fluctuation of 0,2 at the pH results.

The following **conclusions** could be drawn:

- The blank pH differed from the samples, its pH was always slightly under 7,0 and the samples were always a little bit over that. Overall the extraction increases the pH for about 0,5.
- The coldwater and hotwater extractions do not differ from each other at the pH
- Between the samples no differences could be determent. The small fluctuations are more based on the errors of the test than the samples themselves.
- Maybe sample Nr. 4 and 5 might rise the pH a little higher and Nr. 7 a little lower than the others
- This small change in the pH will not make a big difference at making coffee with the filters since the coffee itself influences the pH at a much higher degree towers lower numbers. So the migrated substances might rise the pH for ~0,5 maybe counting the falling of the pH from the coffee itself.

4.5 Results of the potassium permanganate method

4.5.1 Calculation of the organic substance in an extract

Like in the other methods a new extract had to be made for all the samples. Because of different reasons only one test-series with one new coldwater extract could be made (so the results are no average values).

The formula for the determination of the organic substance was provided by the instruction: With the titration the actual amount of used up $KMnO_4$-solution can be measured and with the following coherences

1ml 0,001n $KMnO_4$-solution contains 31,61µg $KMnO_4$.

1mg $KMnO_4$ co responses to 5,25mg organic substance

The formulas for the determinations follow:

$$\text{KMnO4 in the extract} = \frac{\text{ml } 0{,}001\text{n } KMnO_4 \cdot 31{,}61 \cdot \text{Volume of the extract}}{\text{Volume of water in ml}}$$

$$= \frac{\text{ml } 0{,}001\text{n } KMnO_4 \cdot 31{,}61 \cdot 250}{100} = \text{ml } 0{,}001\text{n } KMnO_4 \cdot 31{,}61\text{g} \cdot 2{,}5$$

Formula 3: $KMnO_4$ in the extract

$$\text{Organic substance in the extract} = \text{ml } 0{,}001\text{n } KMnO_4 \cdot 31{,}61 \cdot 2{,}5 \cdot 5{,}25$$

$$= \text{ml } 0{,}001\text{n } KMnO_4 \cdot 414{,}88$$

Formula 4: Organic substance in an extract

In the following tablets the results are summarized:

Table 19: organic substance in the distillate (the volatile substances)

Sample	$KMnO_4$ [ml]	Oxalic acid [ml]	Actual $KMnO_4$ amount [ml]	Organic substance in the extract	[µg/dm²]
1	10,0	0,9	9,2	3796,2	698,5
2	10,0	2,3	7,7	3194,6	574,0
3	10,0	11,3	-1,3	-518,6	-90,0
4	10,0	5,8	4,3	1763,2	310,6
5	10,0	5,8	4,2	1732,1	283,1
6	10,0	5,8	4,3	1763,2	291,1
7	10,0	7,2	2,8	1172,0	211,4
B	10,0	6,1	4,0	1638,8	

Table 20: organic substance in the residue (the non volatile substances)

Sample	$KMnO_4$ [ml]	Oxalic acid [ml]	Actual $KMnO_4$ amount [ml]	Organic substance in the extract	[µg/dm²]
1	80,0	0,7	79,3	32900,0	6053,6
2	60,0	4,1	56,0	23212,5	4171,1
3	40,0	7,0	33,0	13691,0	2377,2
4	30,0	1,1	28,9	11990,0	2111,8
5	40,0	2,3	37,7	15641,0	2556,2
6	40,0	2,4	37,6	15609,9	2577,5
7	60,0	4,1	55,9	23181,4	4181,2
B	30,0	23,0	7,0	2904,2	

The sample Nr. 3 resulted in a wrong number at the distillate because more oxalic acid was used than $KMnO_4$ was provided which cannot be the case.

4.5.2 Discussion of the results

In the following illustrations the amount are shown again, for the wrong result of sample Nr. 3 a very low concentration was give (100 µg/dm²) instead of the negative impossible result:

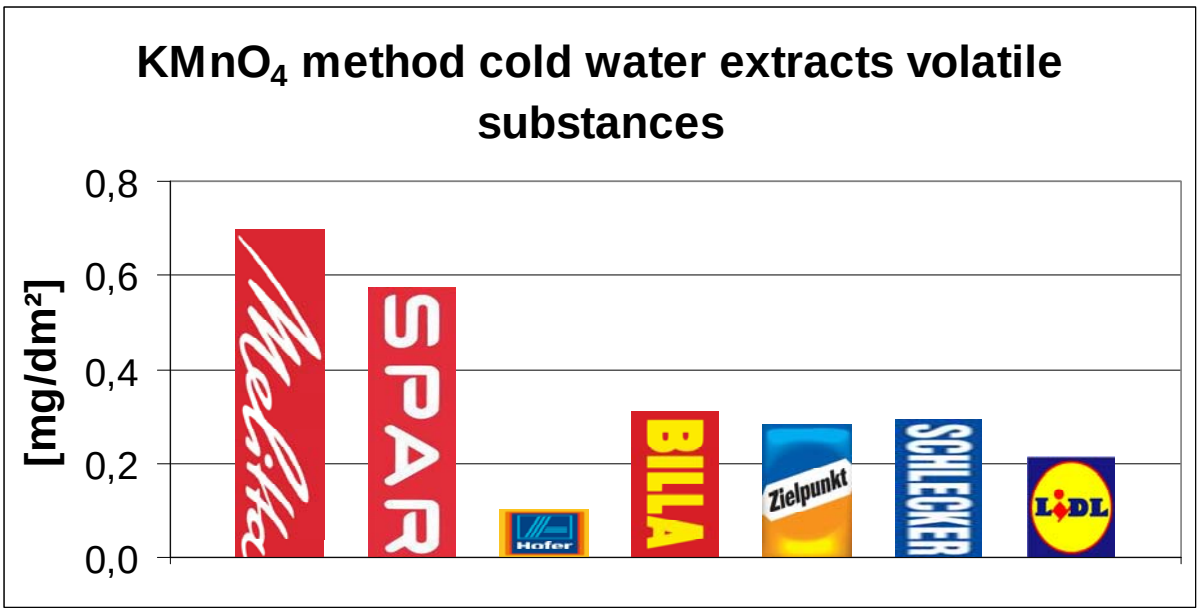

Figure 2: The volatile organic substances in mg/dm²

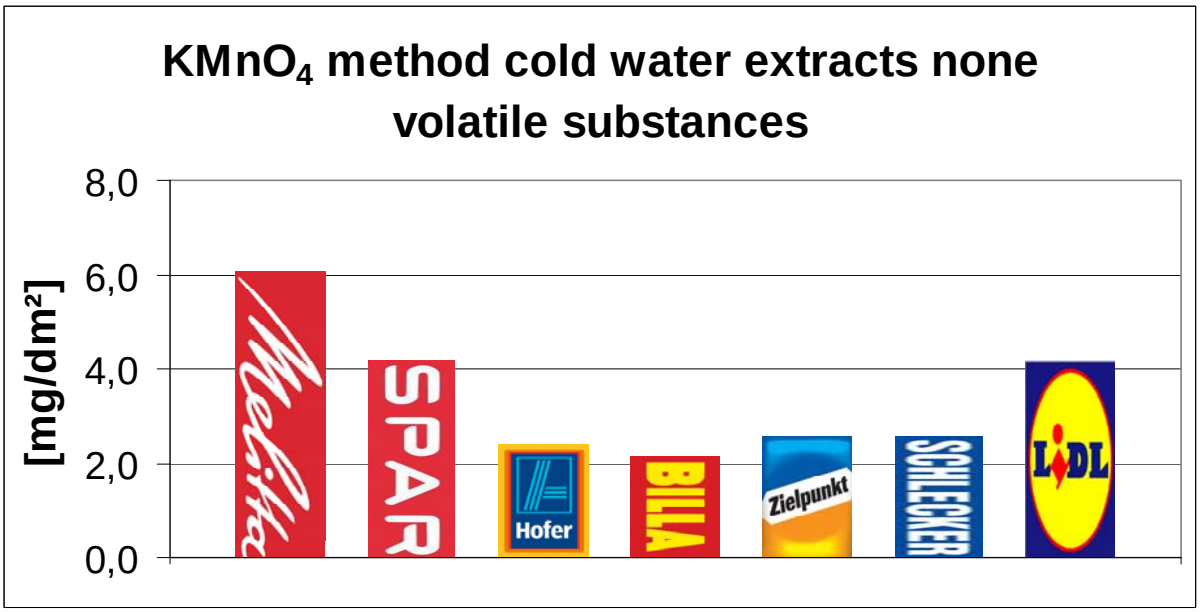

Figure 3: The non volatile organic substances in mg/dm²

The method can only be used for a general overlook of the organic substances in an extract. The titration is not as accurate as other methods.
In the instruction it is only mentioned that the titration should stop when the pink colour is gone. But at the experiment the colour change was not pink to colourless within a few drops but within 5-7ml.
First the pink liquid turned light orange and turned lighter and lighter until the entire colour was gone. The solution wasn't clear at the end but non transparent.

So the exact end of the titration was hard to determent, but a certain point was always chosen for the end so the samples are comparable between each other but the result might be off a little bit overall.

The potassium permanganate was also added in 10ml portions, so at most ~9,9ml oxalic acid could have been used in the titration. This theoretical correlation was also verified by the

experiment expect at the sample Nr. 3 at the distillate. The wrong result can be explained by the former reasons like the wrong final point of the titration.

But the experiment provided the hoped overlook of the organic substances; the following **conclusions** can be drawn:

- In the **distillate** there were not many organic substances, the results were fluctuating and very low, even close to the blank. The differences between the samples are more likely based on the error of the titration method in general. The distillate was also gained with a simple reflux condenser so losses are also possible here. Nevertheless to the 100ml of extract 10ml of potassium permanganate solution were given and the solutions colour pink never went away on its own after heating. Titration was always necessary.
- Only sample Nr. 1 really seems to have the highest result.

- In the **residue** more reliable results could be gained. The blank was much lower than the numbers of the extracts, so a comparison between the samples can be drawn:
- Sample Nr. 3, 4, 5 and 6 got nearly identical results
- Sample Nr 2 and 7 had a much higher result
- And again sample Nr. 1 showed the highest number of non volatile organic substances

4.6 Results of the determination of glyoxal content

4.6.1 The reference curve

With the Titration of the standard solution the actual glyoxal content in it could be determent, the following formula provided by the DIN instruction was used:

$$Glyoxal = \frac{a \times 58{,}016 \times 100}{2 \times m_E \times 1000}$$

Formula 5: Calculation fort he glyoxal % in the solution

a…Used sodium hydroxide solution (1 mol/l), minus the blank (1,8ml) [ml]
m_E…initial weight of the glyoxal solution [g]

Table 21: Results of the glyoxal titration

m_E [g]	a [ml]	glyoxal concentration [%]
0,9945	12,3	35,88
0,9925	12,4	36,24
1,0246	12,8	36,24

For the later calculations the average value for the glyoxal concentration of 36,12% for the standard solution was used.

In the next tablet die actual concentrations for the 5, 10, 20 and 30 µg solutions was calculated with the information of the actual glyoxal concentration, the corresponding result of the Absorbance is also listed:

Table 22: Results of the reference curve

glyoxal [µg]	absorbance
5,88	0,117

11,76	0,530
23,53	0,782
35,65	1,244

As mentioned under 3.9.4.1 the results of the lower glyoxal concentrations were not included, they are not that reliable but they did not change the reference curve much anyway.

In the following image the reference curve for the used glyoxal standard in combination with the photometer is displayed:

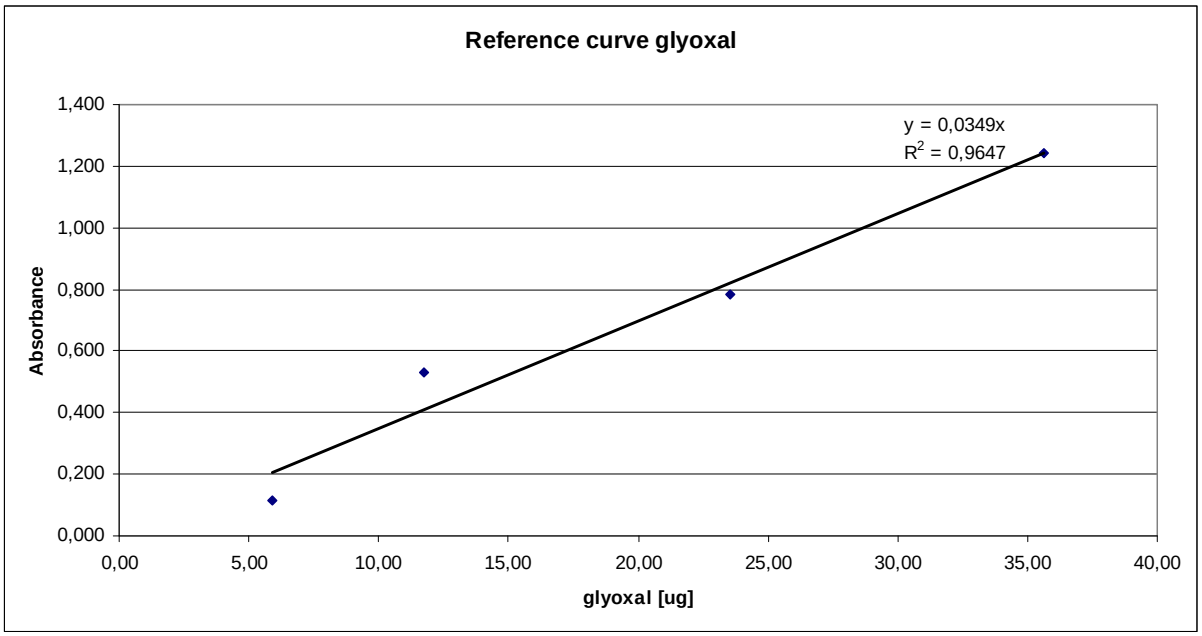

Figure 4: Reference curve for glyoxal

4.6.2 Results of the coldwater extracts

In the following tablet the results of the first and second series of coldwater extracts is shown:

Table 23: Data of the coldwater extracts

1. test-series	absorbance	glyoxal [µg]	2.test-series	absorbance	glyoxal [µg]
1	0,022	0,61	1	0,012	0,33
2	0,034	0,94	2	0,045	1,25
3	0,018	0,50	3	0,021	0,58
4	0,018	0,50	4	0,015	0,42
5	0,033	0,91	5	0,038	1,05
6	0,055	1,52	6	0,035	0,97
7	0,028	0,78	7	0,024	0,66

In the next tablet the average values for the glyoxal content in the coldwater extracts are listed:

Table 24: Average value of the glyoxal content of the coldwater extracts

Sample	average value glyoxal [µg]
1	0,47
2	1,09
3	0,54
4	0,46

5	0,98
6	1,25
7	0,72

With those results, the results from previous tests and the formula provided by the DIN instructions the soluble glyoxal content in mg/kg (C_m) or mg/dm² (C_s) can be calculated:

$$C_m = C \times \frac{V_0}{V_1} \times \frac{1}{G} \times \frac{100}{100 - f} \times 1000$$

Formula 6: Glyoxal [mg/kg] content in the extract

$$C_S = C \times \frac{V_0}{V_1} \times \frac{b}{100} \times \frac{1}{G} \times \frac{100}{100 - f}$$

Formula 7: Glyoxal [mg/dm²] content in the extract

C…mass fraction determent with the photometer [mg]
V_0…the volume of the extracts (250ml) [ml]
V_1…the analysed part of the extracts (25ml) [ml]
b…area related mass (4.2) [g/m²]
G…the weight of the sample at preparation of the extract (10g) [g]
f…the moisture content of the sample (4.1) [%]

In the next table the used data for the calculation is summarized:

Table 25: Data for the calculation

Sample	G [g]	f [%]	1 filter [g]	1 filter dm²	b [g/m²]
1	10,00	1,0	1,84	2,875	64,00
2	10,00	1,1	1,80	2,875	62,50
3	10,00	1,2	1,74	2,875	60,39
4	10,00	1,2	1,76	2,875	61,26
5	10,00	0,6	1,63	2,875	56,85
6	10,00	0,2	1,65	2,875	57,43
7	10,00	0,0	1,80	2,875	62,74

So the final result of the actual soluble glyoxal content in the extract can be determent:

Table 26: Results of the coldwater extracts

Sample	C_m [mg/kg]	C_s [mg/dm²]
1	0,49	0,0003
2	1,13	0,0007
3	0,56	0,0003
4	0,47	0,0003
5	1,01	0,0006
6	1,27	0,0007
7	0,73	0,0005

4.6.3 Control test of the glyoxal content

Except the lower volume, the extraction followed the same steps as described in 3.4, the compared results are shown in the next tablet:

Table 27: Comparison of the cold water extracts of sample Nr. 6

1. test-series	Absorbance	glyoxal [µg]	2. test-series	Absorbance	glyoxal [µg]	average value [µg]
6 (200ml)	0,055	1,52	6 (200ml)	0,035	0,97	1,25
6 (100ml)	0,062	1,72	6 (100ml)	0,085	2,35	2,03

The fluctuations between the repeated determinations are high themselves. But at the numbers show, that the absorbance signal is higher in general. When the factor 2 from the liquid volume is factored in the calculation the resulting concentration is nearly the same, as shown in the next tablet:

Table 28: Glyoxal content of the control test

Sample	av. C_s [mg/dm²]
6 (200ml)	0,0007
6 (100ml)	0,0006

This comparison is also shown in the next image:

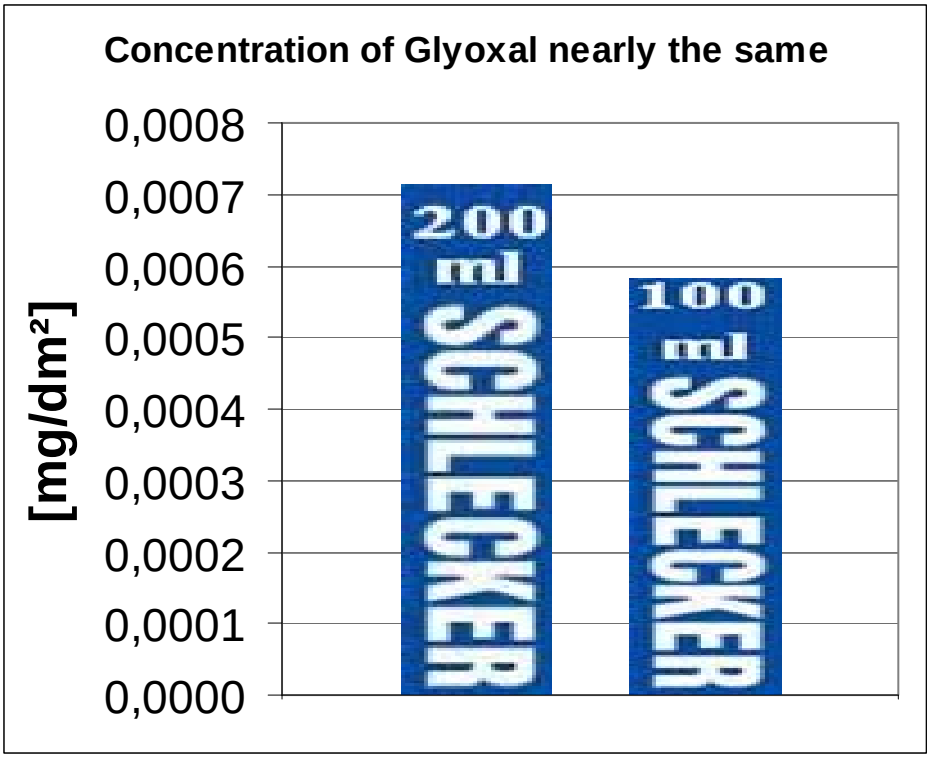

Figure 5: Graphical comparison of the control test

In the end nearly the same concentration was calculated. The small differences between the two tests could be a result in the errors of the method itself at the extraction preparation, the preparation of the samples for the photometer or at the photometer itself.
The method is also based on the extraction with 200ml, 100ml covert all the paper but not as well as 200ml, so maybe a little less glyoxal was extracted, resulting in a lower result.

4.6.4 Results of the hotwater extracts

The calculations with the hotwater extracts followed the same concept as in 4.6.2 with the coldwater extracts explained. In the next tablet the results of the first and the second test-series are listed:

Table 29: Data of the hotwater extracts

1. test-series	absorbance	glyoxal [µg]	2.test-series	absorbance	glyoxal [µg]
1	0,045	1,25	1	0,047	1,30
2	0,052	1,44	2	0,036	1,00
3	0,057	1,58	3	0,053	1,47
4	0,049	1,36	4	0,049	1,36
5	0,052	1,44	5	0,044	1,22
6	0,071	1,97	6	0,057	1,58
7	0,040	1,11	7	0,041	1,14

The next table shows the average values for the glyoxal content in the hotwater extracts:

Table 30: Average value of the glyoxal content of the coldwater extracts

Sample	average value glyoxal [µg]
1	1,27
2	1,22
3	1,52
4	1,36
5	1,33
6	1,77
7	1,12

And in the next chart the final results are summarized:

Table 31: Results of the hotwater extracts

Sample	C_m mg/kg	C_s mg/dm²
1	1,2868	0,0008
2	1,2314	0,0008
3	1,5420	0,0009
4	1,3726	0,0008
5	1,3373	0,0008
6	1,7757	0,0010
7	1,1213	0,0007

4.6.5 Discussion of the results

For the discussion of the results, the final numbers of all the extracts are listed again in the following table:

Table 32: Summary of the glyoxal content results

Sample	Coldwater extracts C_m [mg/kg]	Hotwater extracts C_m [mg/kg]	Coldwater extracts C_s [mg/dm²]	Hotwater extracts C_s [mg/dm²]
1	0,48	1,29	0,0003	0,0008
2	1,11	1,23	0,0007	0,0008
3	0,55	1,54	0,0003	0,0009
4	0,46	1,37	0,0003	0,0008
5	0,99	1,34	0,0006	0,0008
6	1,25	1,78	0,0007	0,0010
7	0,72	1,12	0,0005	0,0007

The summary is also shown graphical in the next figure:

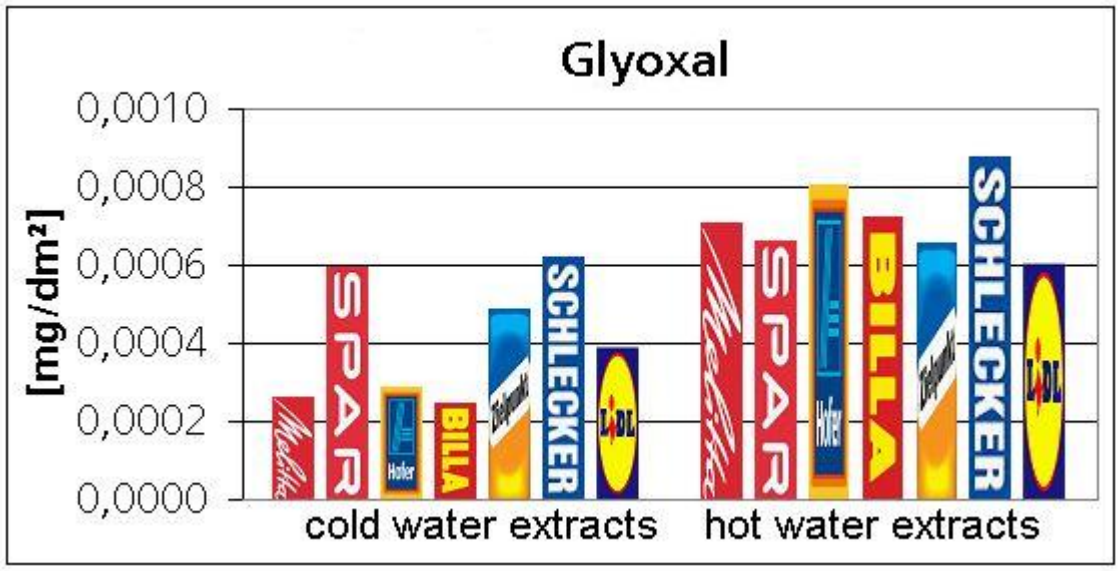

Figure 6: Results of the coldwater and hotwater extracts

The possible **sources of errors** were already mentioned. The extracts themselves might differ a little bit; an average value from one repeated determination might counter this a little bit.

The control test showed that an error might be possible but the general picture of very low concentrations and repeatable results was confirmed.

So the following conclusions concerning the glyoxal content that might migrate from the filter paper can be drawn:

- The control test showed very well that there is indeed a change from the blanks and a concentration of glyoxal is present in the extract. The instructions mention that formaldehyde should not influence the result, but maybe other aldehydes could give a similar (yellow) product and at so low numbers they might influence the test.
- The absorbance numbers are very low but assuming the soluble glyoxal content is really shown accurate it seems to be very low. The safety limit given by is 1,5 mg/dm². (48) So the content is lower than the safety limit by a factor of 1500 to 2500
- The hotwater extracts result in a higher concentrations, so more glyoxal is extracted as expected with the use of heating.
- Between the samples there are some differences but all on such a small level that they can nearly be ignored. The only general result could be that sample Nr. 6 shows the highest concentration at both extraction methods.

4.7 Results of the determination of formaldehyde content

4.7.1 The reference curve

The concentration of the formaldehyde-solution was designated by the titration. On average 27,5ml thiosulfate were used, with this result the concentration could be calculated:

27,5ml thiosulfate (c=0,1mol/l) relate to 0,00275mol thiosulfate

Those react in the following way:

$$2S_2 + O_3^{2-} \rightarrow S_4O_6 + 2e^-$$
$$I_2 + 2e^- \rightarrow 2I^-$$
$$2Na_2S_2O_3 + I_2 \rightarrow S_4O_6 + NaI$$

Formula 8: Reaction of the thiosulfate at the titration

Because two thiosulfate molecules are necessary, they equal 0,001375mol iodine.

25ml iodine (c=0,05mol/l) were used, which equal 0,00125mol iodine.

The difference is 0,000125mol, which equals 3,75mg formaldehyde
(formaldehyde…30g/mol)

This result was gained with the following hint of the DIN instructions:

1,0ml iodine (c=0,05mol/l) equal 1,5mg formaldehyde
So 2,5ml (=27,5ml-25ml) equal 3,75mg formaldehyde

10ml of the 1000ml formaldehyde-solution were used which result in a concentration of **37,5%** or 375 g/l.

In the following table the absorbance of the used reference solutions are listed with the actual formaldehyde content following the result of the titration:

Table 33: Content of the reference solutions

reference solutions	formaldehyde [ug]	absorbance
1	0,94	0,013
5	4,69	0,044
10	9,38	0,085
15	14,06	0,120
20	18,75	0,159
25	23,44	0,195

In the following illustration the resulting reference curve is shown:

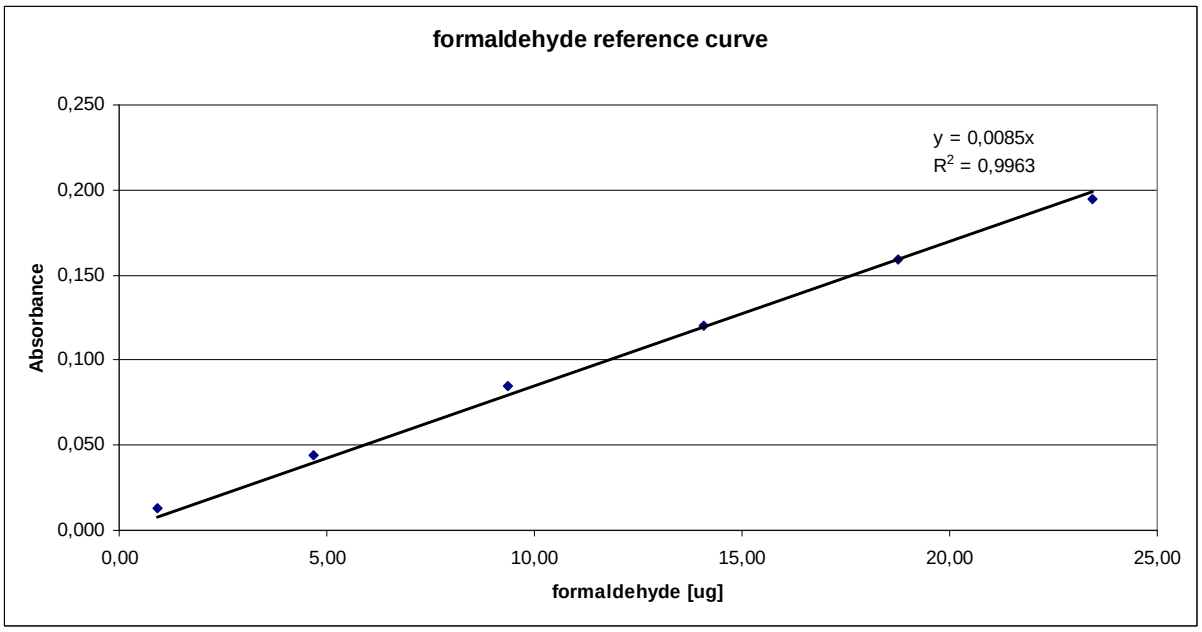

Figure 7: Formaldehyde reference curve

4.7.2 Results of the coldwater extracts

In the next chart the data of the 1. and the 2. test-series of the coldwater extracts are listed:

Table 34: Data of the coldwater extracts

1. test-series	absorbance	formaldehyde [ug]	2. test-series	absorbance	formaldehyde [ug]
1	0,020	2,35	1	0,023	2,71
2	0,035	4,12	2	0,056	6,59
3	0,015	1,76	3	0,019	2,24
4	0,029	3,41	4	0,046	5,41
5	0,034	4,00	5	0,041	4,82
6	0,053	6,24	6	0,062	7,29
7	0,020	2,35	7	0,024	2,82

In the following table the resulting average values are shown:

Table 35: Average value of the coldwater extracts

Sample	Average value formaldehyde [ug]
1	2,53
2	5,35
3	2,00
4	4,41
5	4,41
6	6,76
7	2,59

This data set combined with previous test and the formula provided by the DIN instructions can be used to calculate the soluble formaldehyde content in mg/kg (C_m) or mg/dm² (C_s).

$$C_m = C \times \frac{V_0}{V_1} \times \frac{1}{G} \times \frac{100}{100 - f} \times 1000$$

Formula 9: Formaldehyde [mg/kg] content in the extract

$$C_S = C \times \frac{V_0}{V_1} \times \frac{b}{100} \times \frac{1}{G}$$

Formula 10: Formaldehyde [mg/dm²] content in the extract

C…mass fraction determent with the photometer [mg]
V_0…the volume of the extracts (250ml) [ml]
V_1…the analysed part of the extracts (25ml) [ml]
b…area related mass (4.2) [g/m²]
G…the weight of the sample at preparation of the extract (10g) [g]
f…the moisture content of the sample (4.1) [%]

The used data set is already summarized at the glyoxal calculations and the next table shows the final results for the formaldehyde content:

Table 36: Results from the coldwater extracts

Sample	C_m [mg/kg]	C_s [mg/dm²]
1	2,56	0,0016
2	5,41	0,0033
3	2,03	0,0012
4	4,46	0,0027
5	4,44	0,0025
6	6,78	0,0039
7	2,59	0,0016

4.7.3 Results of the hotwater extracts

In next chart lists the data of the first and the second hotwater test-series:

Table 37: Data of the hotwater extracts

1. test-series	absorbance	formaldehyde [ug]	2. test-series	absorbance	formaldehyde [ug]
1	0,045	5,29	1	0,047	5,53
2	0,052	6,12	2	0,036	4,24
3	0,057	6,71	3	0,053	6,24
4	0,049	5,76	4	0,049	5,76
5	0,052	6,12	5	0,044	5,18
6	0,071	8,35	6	0,057	6,71
7	0,040	4,71	7	0,041	4,82

The average values based on this data is summarized in the next table:

Table 38: Average value of the hotwater extracts

Sample	average value formaldehyde [ug]
1	5,41
2	5,18
3	6,47
4	5,76
5	5,65
6	7,53
7	4,76

Analog to the coldwater extracts the results for the soluble formaldehyde content can be calculated:

Table 39: Formaldehyde content in the hotwater extracts

Sample	C_m [mg/kg]	C_s [mg/dm²]
1	5,4682	0,0035
2	5,2327	0,0032
3	6,5525	0,0039
4	5,8326	0,0035
5	5,6825	0,0032
6	7,5454	0,0043
7	4,7647	0,0030

4.7.4 Discussion of the results

Again the data is collectively shown in the next chart:

Table 40: Summary of the formaldehyde content results

Sample	Coldwater extracts C_m [mg/kg]	Hotwater extracts C_m [mg/kg]	Coldwater extracts C_s [mg/dm²]	Hotwater extracts C_s [mg/dm²]
1	2,56	5,47	0,0016	0,0035
2	5,41	5,23	0,0033	0,0032
3	2,03	6,55	0,0012	0,0039
4	4,46	5,83	0,0027	0,0035
5	4,44	5,68	0,0025	0,0032
6	6,78	7,55	0,0039	0,0043
7	2,59	4,76	0,0016	0,0030

The figure shows the results graphically:

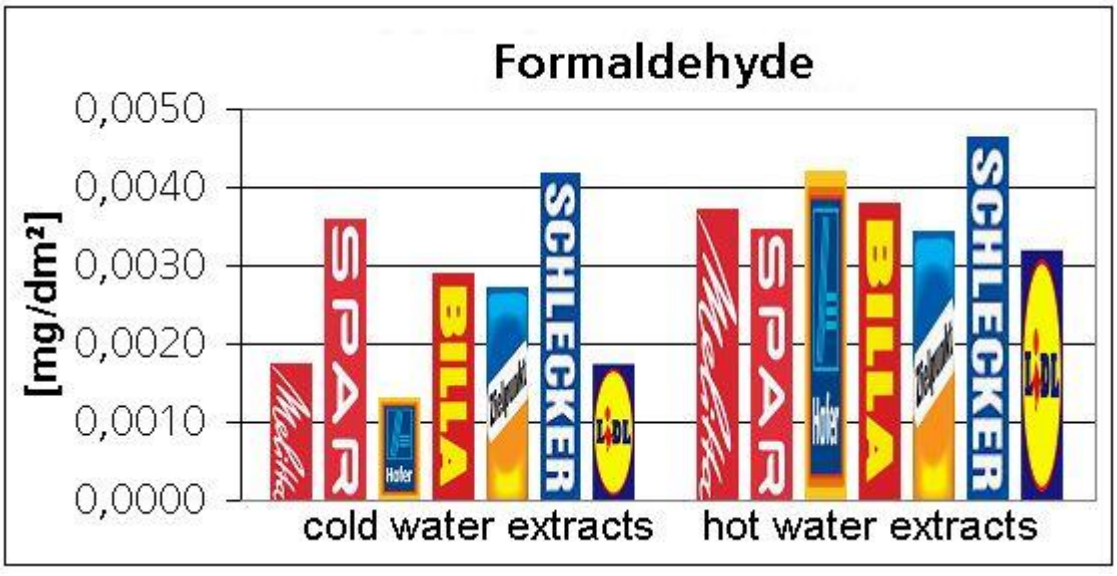

Figure 8: Summary of the formaldehyde content results

The **error sources** stay nearly the same compared to the glyoxal content since the experiment is very similar.

No control test was done here because the absorbance levels were within the points of the instructed reference curve and the resulting concentrations are also higher than at glyoxal.

The instruction do not mention any influences from other aldehydes or glyoxal but the method should only show the formaldehyde content since is based on a very typical organic reaction for this compound.

The following **conclusions** concerning the formaldehyde content that might migrate from the filter paper can be drawn:

- The absorbance numbers are low but assuming the soluble formaldehyde content is really shown accurate it seems to be low too. The safety limit given by is 1,0 mg/dm² (48). So the content is lower than the safety limit by a factor of 200 to 300.
- The hotwater extracts result in a higher concentrations, but not as exact as the comparison with the glyoxal extracts. For example sample Nr. 2 and 6 showed nearly the same concentration in both extraction methods.
- Between the samples there are some differences but again all on a small level. It is interesting that sample Nr. 6 showed the highest results again.

4.8 Results of the determination of pentachlorophenol content

4.8.1 The reference curve

The four prepared solutions resulted in the following data:

Table 41: Data for the pentachlorophenol determination

reference solutions	pentachlorophenol [ug]	absorbance
1	0,005	0,007
2	0,01	-0,072
3	0,02	-0,007
4	0,04	-0,166

The data was not useable, the concentration had to be higher compared to the blank, but sadly this could not be observed. If no organic reaction took place, the solutions should give the same result as the blank. This data suggest, that nothing of significances was measured but only random fluctuations compared to the blank.

4.8.2 Results of the coldwater extracts

In the upcoming chart the experimental data of the determination is displayed:

Table 42: Results of the pentachlorophenol determination

1. test-series	absorbance	2. test-series	absorbance	av. absorbance
1	-0,329	1	-0,157	-0,243
2	-0,086	2	-0,261	-0,174
3	0,064	3	-0,032	0,016
4	0,126	4	0,238	0,182
5	0,159	5	-0,015	0,072
6	0,098	6	0,396	0,247
7	0,244	7	0,325	0,285

Again the data was not really useable, since some results were lower than the blank and the results were not reproducible with the second determination.

4.8.3 Discussion of the results

Without a reference curve the data can not be calculated and even if a reference curve would have been available the data suggests that the method simply did not work as the instructions suggest.

The first reason for that could be that the instructions were only found in this book, no other alternative photometric measurement of the pentachlorophenol content could be found and this test is also based on a 50 year old instruction.

The volumes were not given by the instructions, so maybe a mistake was used there with the amount of the used reagents at the determination of the sample-content.

At the reference curve only two reagents were added but again the amount was chosen based on experience and not on any instruction. There the problem also occurred that the standard was based on methanol. So maybe the methanol should have been evaporated the same way as the ether at the instruction.
But since very small volumina were used the error would be far too great and the resulting reference curve would be useless.

So sadly this determination did not work. At all the other references the pentachlorophenol content should be determent with the use of a gas chromatograph. So this was done in a later experiment.

4.9 Results of the Scanning Electron Microscope

All images were taken at 20kV; the enlargement is shown at the figure-description.

4.9.1 The images of sample Nr. 1

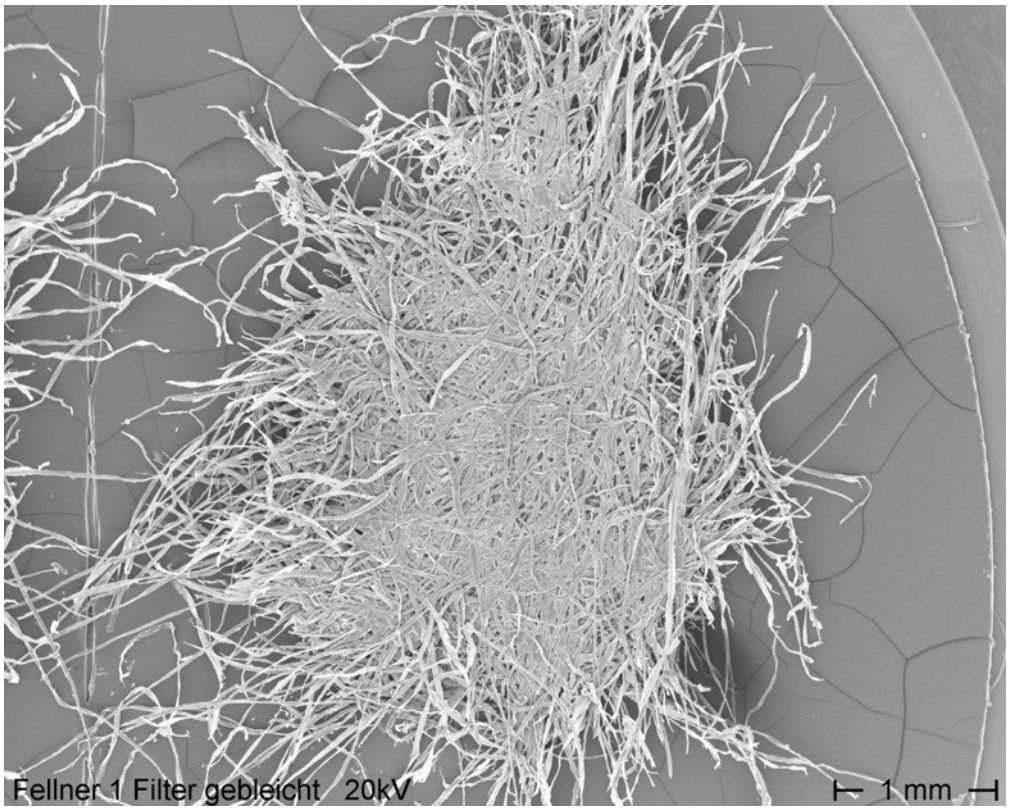

Figure 9: Sample Nr. 1 (bleached) 1mm scale

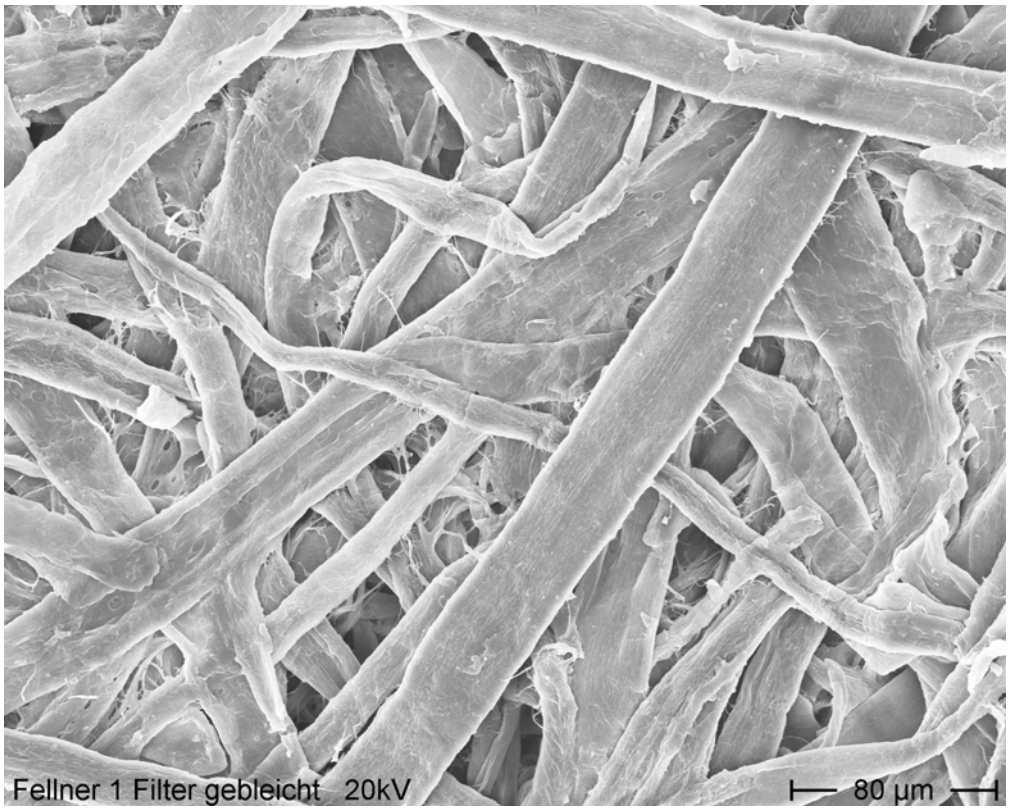

Figure 10: Sample Nr. 1 (bleached) 80µm scale

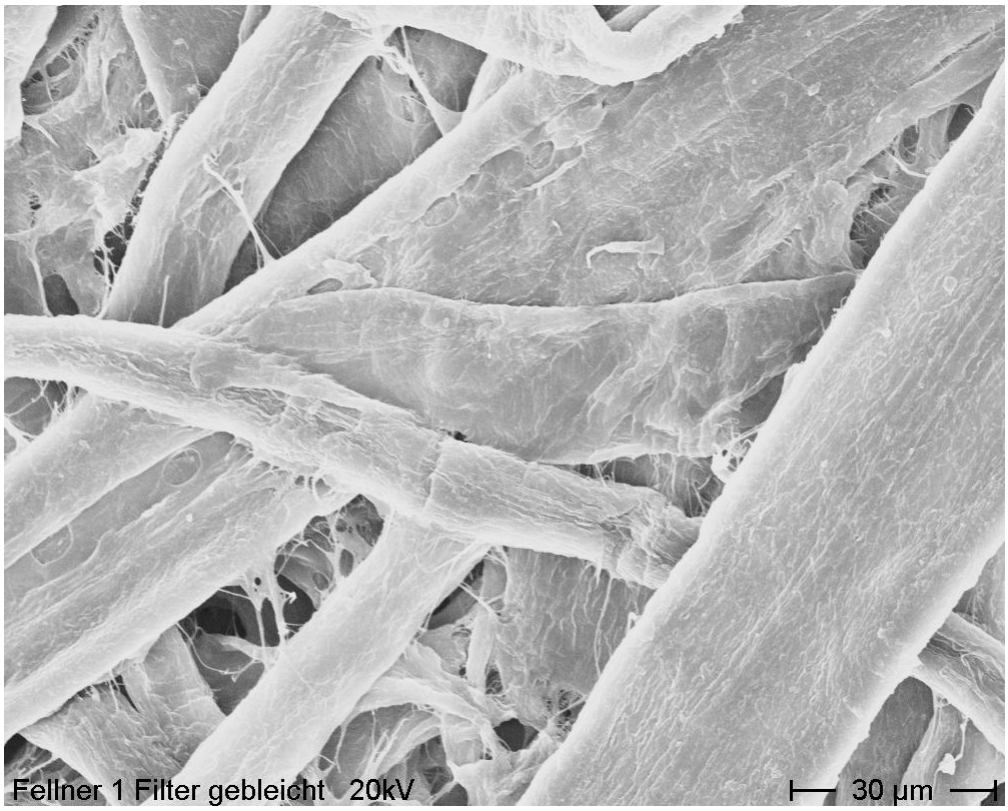

Figure 11: Sample Nr. 1 (bleached) 30µm scale

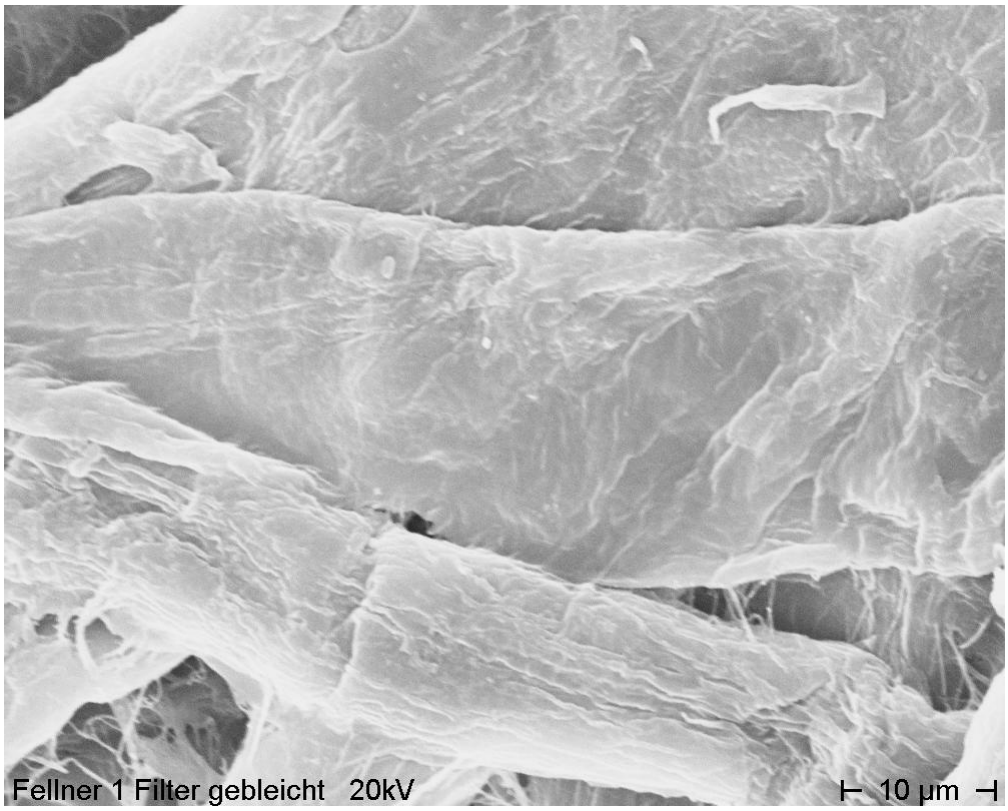

Figure 12: Sample Nr. 1 (bleached) 10µm scale

4.9.2 The images of sample Nr. 4

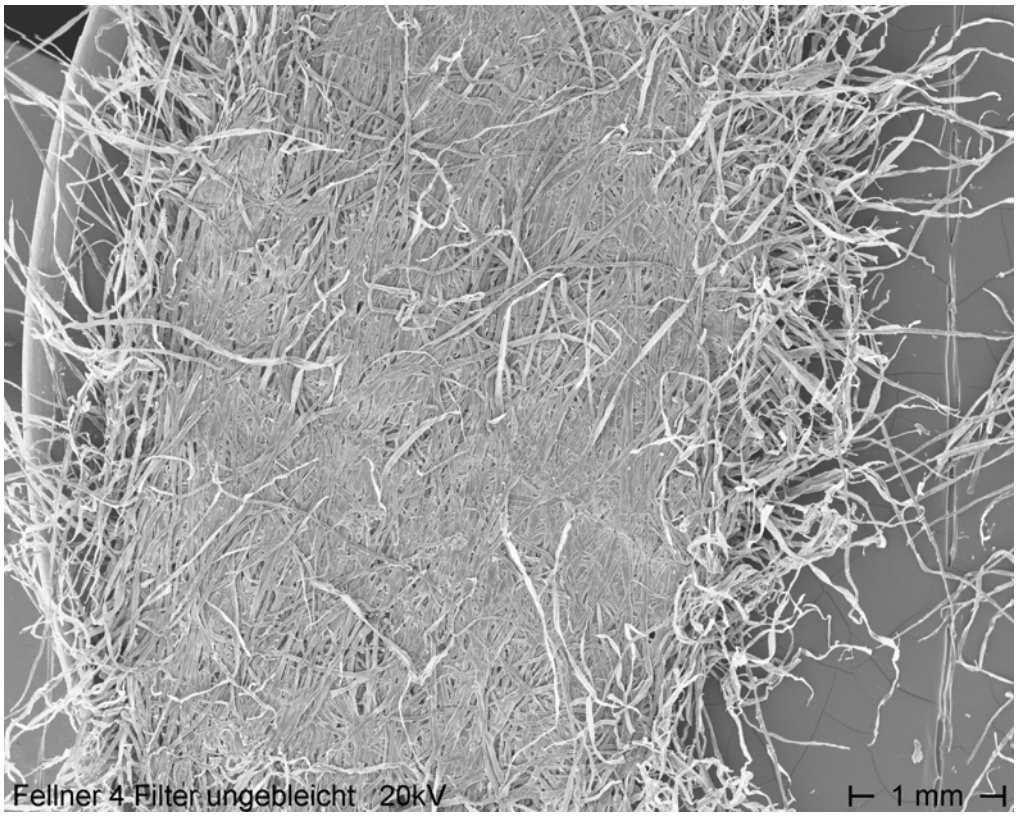

Figure 13: Sample Nr. 4 (unbleached) 1mm scale

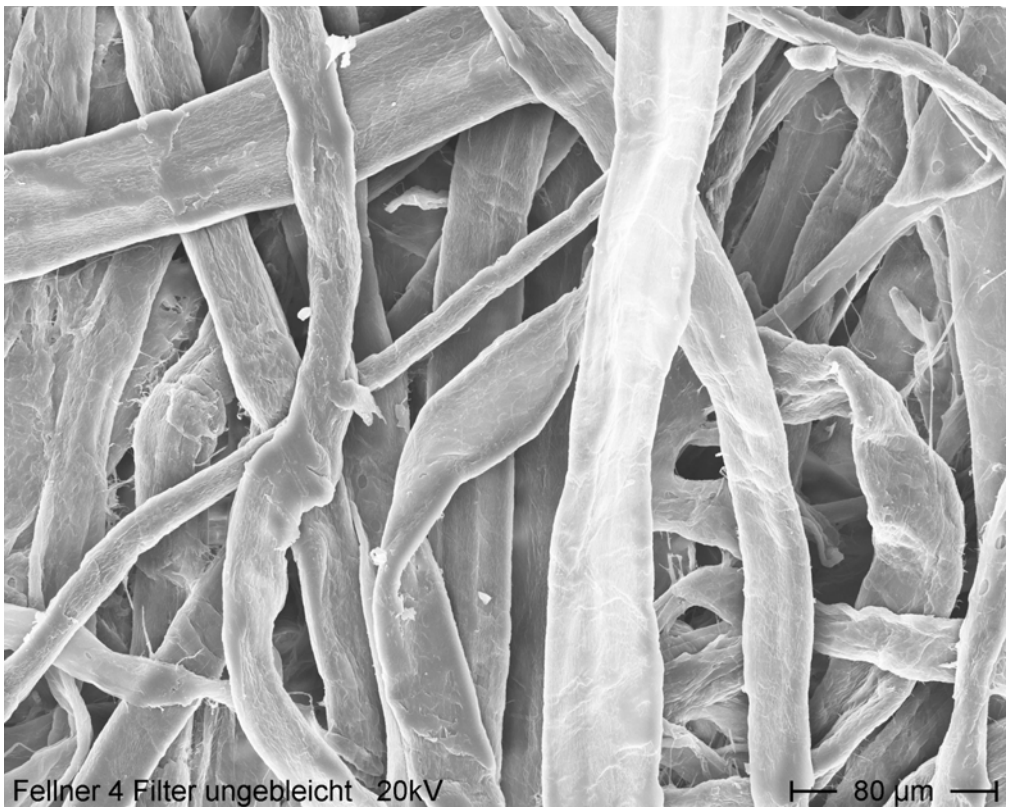

Figure 14: Sample Nr. 4 (unbleached) 80µm scale

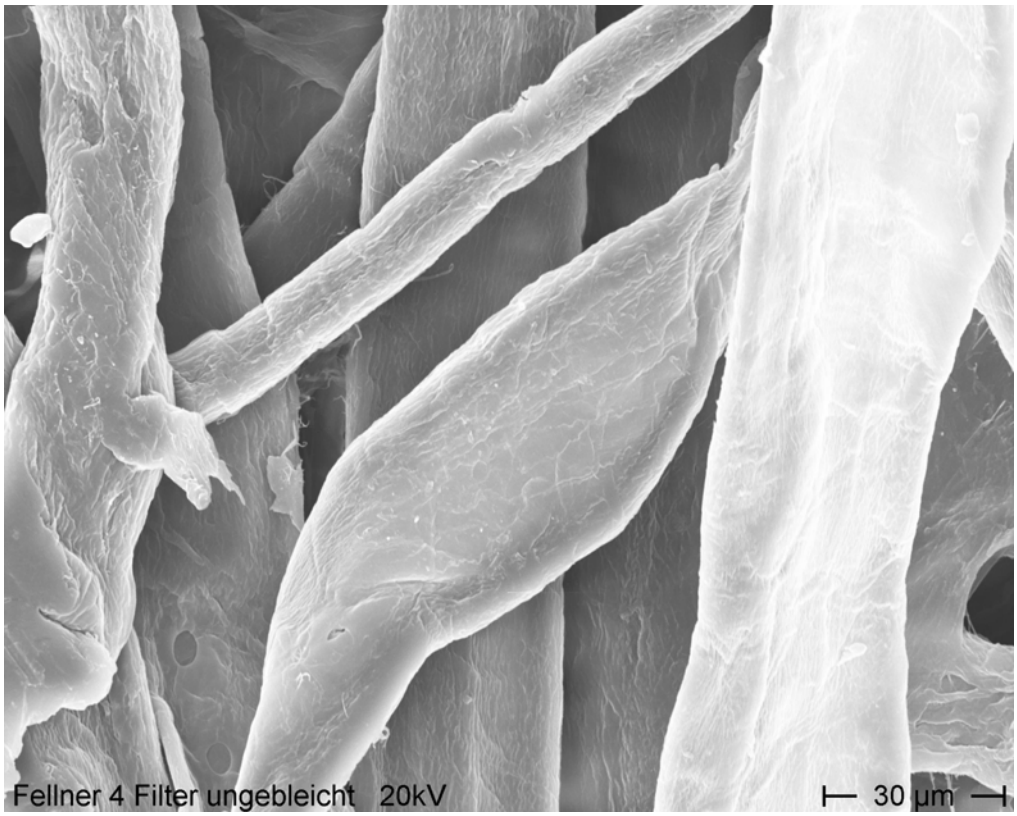

Figure 15: Sample Nr. 4 (unbleached) 30µm scale

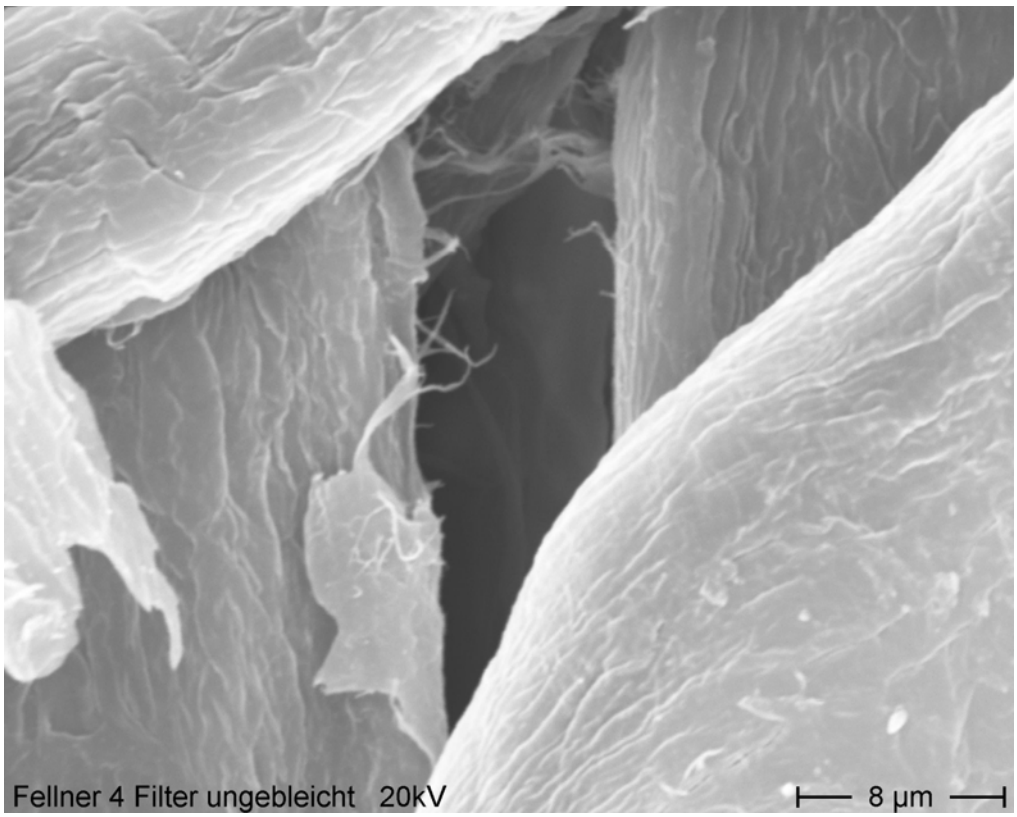

Figure 16: Sample Nr. 4 (unbleached) 8µm scale

4.9.3 Discussion of the images

The objective was to see if there were any other contaminations present than the paper fibers and if there were differences between the bleached and unbleached paper.

The 1mm scale showed that both filters had a very similar paper structure. No big contamination substances could be determent, everything seemed to be part of the paper fibers.
In greater enhancements the paper structure could be seen in greater detail. Again no big junks of any other matter were present. When getting to really small details the surface of the paper fibers could be displayed in greater detail. It is hard to say if any contaminations were present on top of the fibers or if this was just the natural structure.

Overall the **conclusion** can be drawn from those images that there is no difference between the bleached and unbleached filter concerning the paper structure. And there is no indication that larger contaminations are present within the paper, like migrating substances from the packages. In general all pictures display a clean paper structure.

4.10 Results of the Headspace Gas Chromatography – Mass Spectrometry

4.10.1 Results of the untreated filter papers

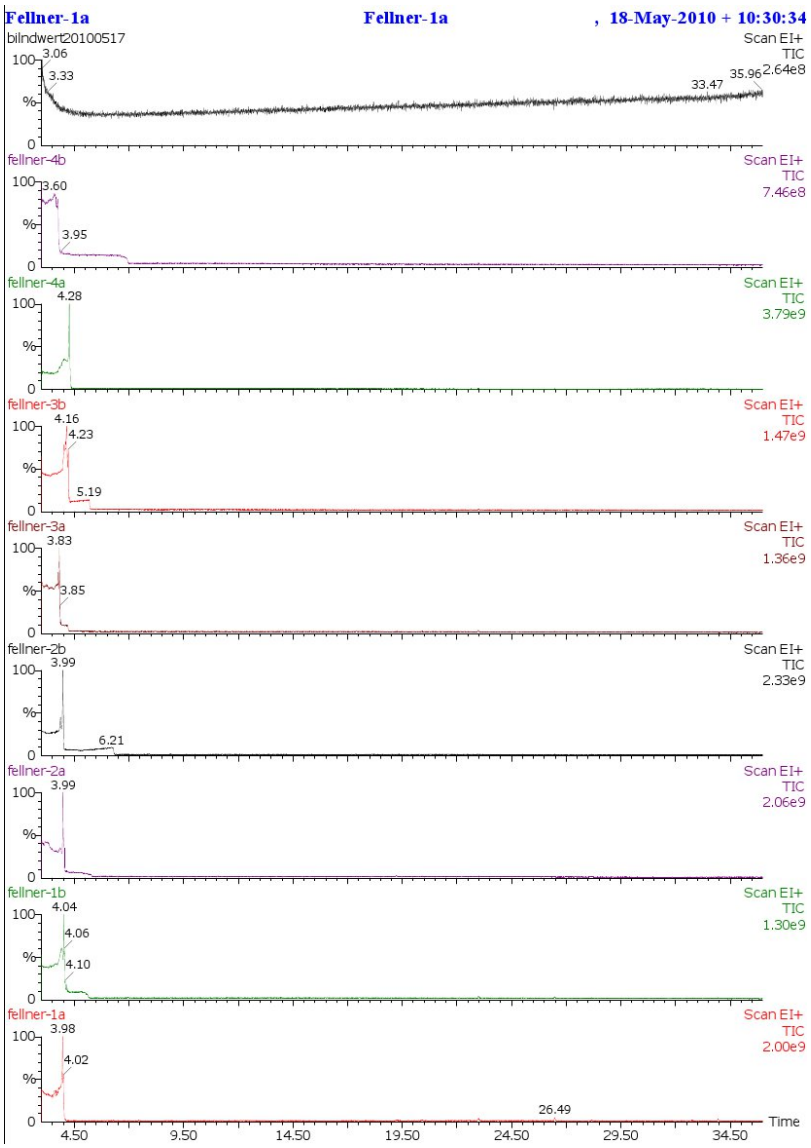

Figure 17: Sample 1 to 4 (with repeated series) and the blank

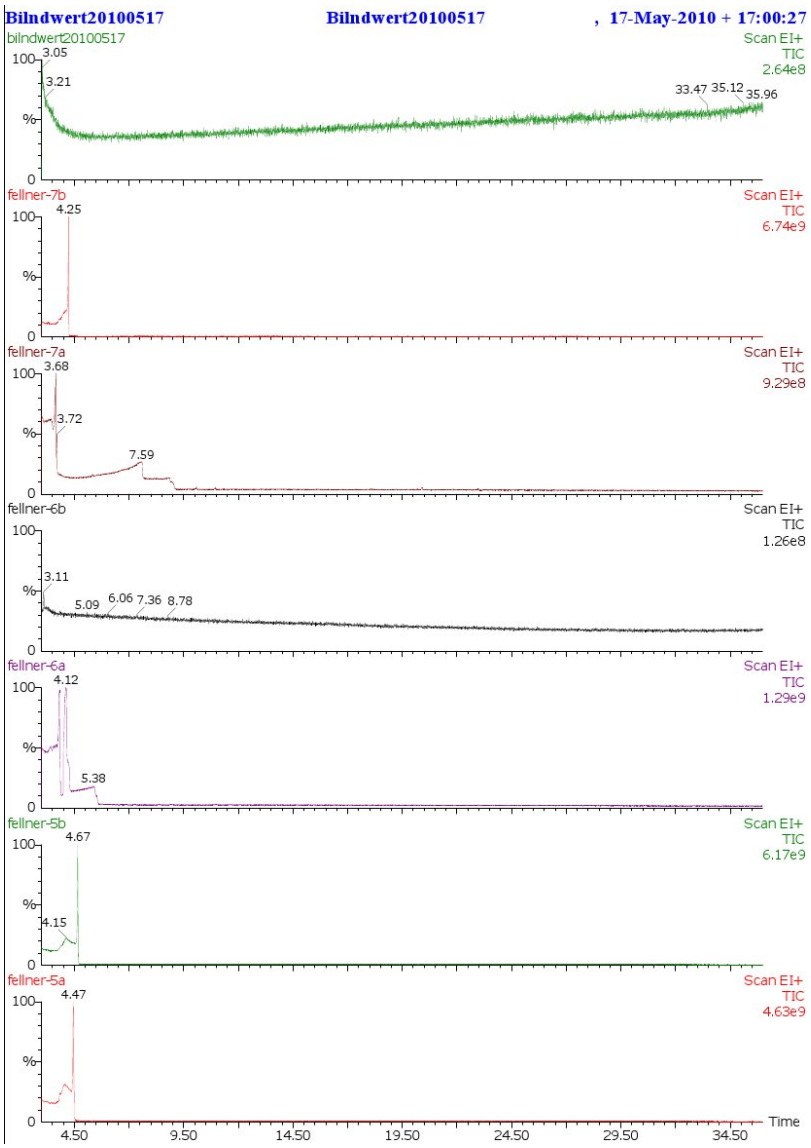

Figure 18: Sample 5 to 7 (with repeated series) and the blank

The chromatograms showed nearly no peaks at all. The intensive peak around 4 minutes is always the air-peak, after 5 to 6 minutes the sample peaks would show. But except a very small peak at sample Nr. 1 at 26,49 minutes, no peaks are listed in the original format.

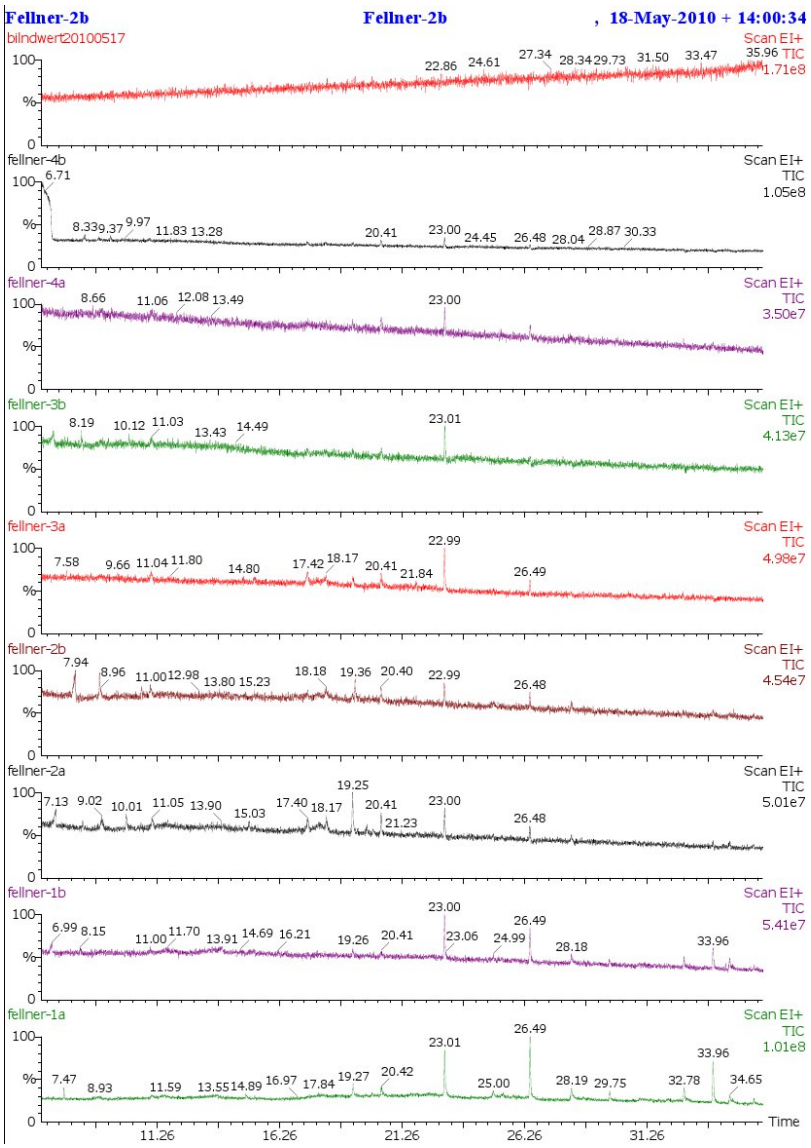

Figure 19: Enhancement after the 7. minute for sample 1 to 4 (with repeated series) and the blank

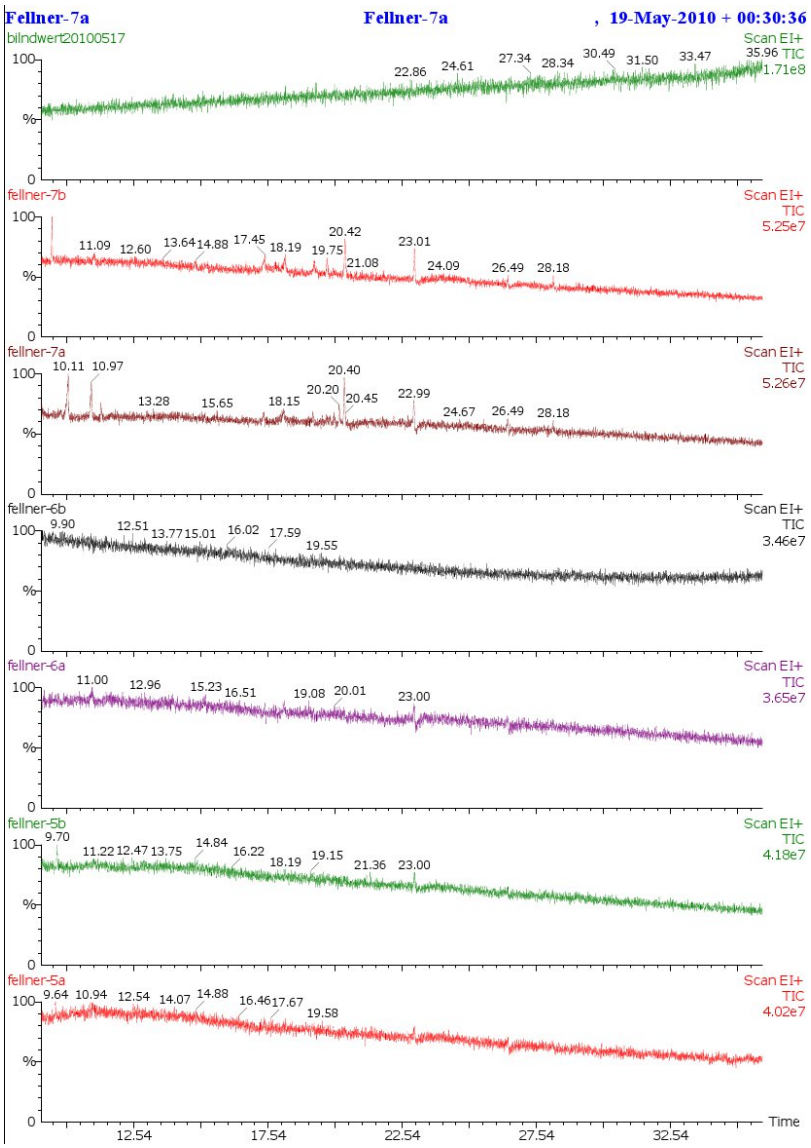

Figure 20: Enhancement after the 7. minute for sample 5 to 7 (with repeated series) and the blank

The chromatogram was enhanced after the 7. minute to show the relevant peaks in greater detail:

- In nearly all samples (1 to 7) a small peak at around **23,00** minutes could be found.
- In sample Nr. 1, 2, 3 and 7 a peak at around **26,49** is seen.
- In sample Nr. 1 an additional peak at **33,96** is shown.
- Sample Nr. 5 and 6 show the least peaks, the 23,00 peak is hardly noticeable
- Sample Nr. 7 differs a little bit from the others with additional peaks
- All the other peaks are even smaller and might just be background noise

Sadly none of the mentioned peaks could be clarified with the internal library of the mass spectrometer. The peaks were too small to give a good specific spectre which could lead to a substance with the library. The spectre offered a too unspecific range of possible substances for the peaks so in the end none could be clarified.

But overall the **conclusion** can be drawn that the untreated filter-papers are clean. No vaporable substances until 150°C could be observed. Specially recycled paper should show some specific organic substances with this method.

So these experiments show that most likely no recycled paper was used for the filters and no substances are migrating from the packaging. This last result was confirmed with the analyses of the packages as well.

4.10.2 Results of the extracted filter papers

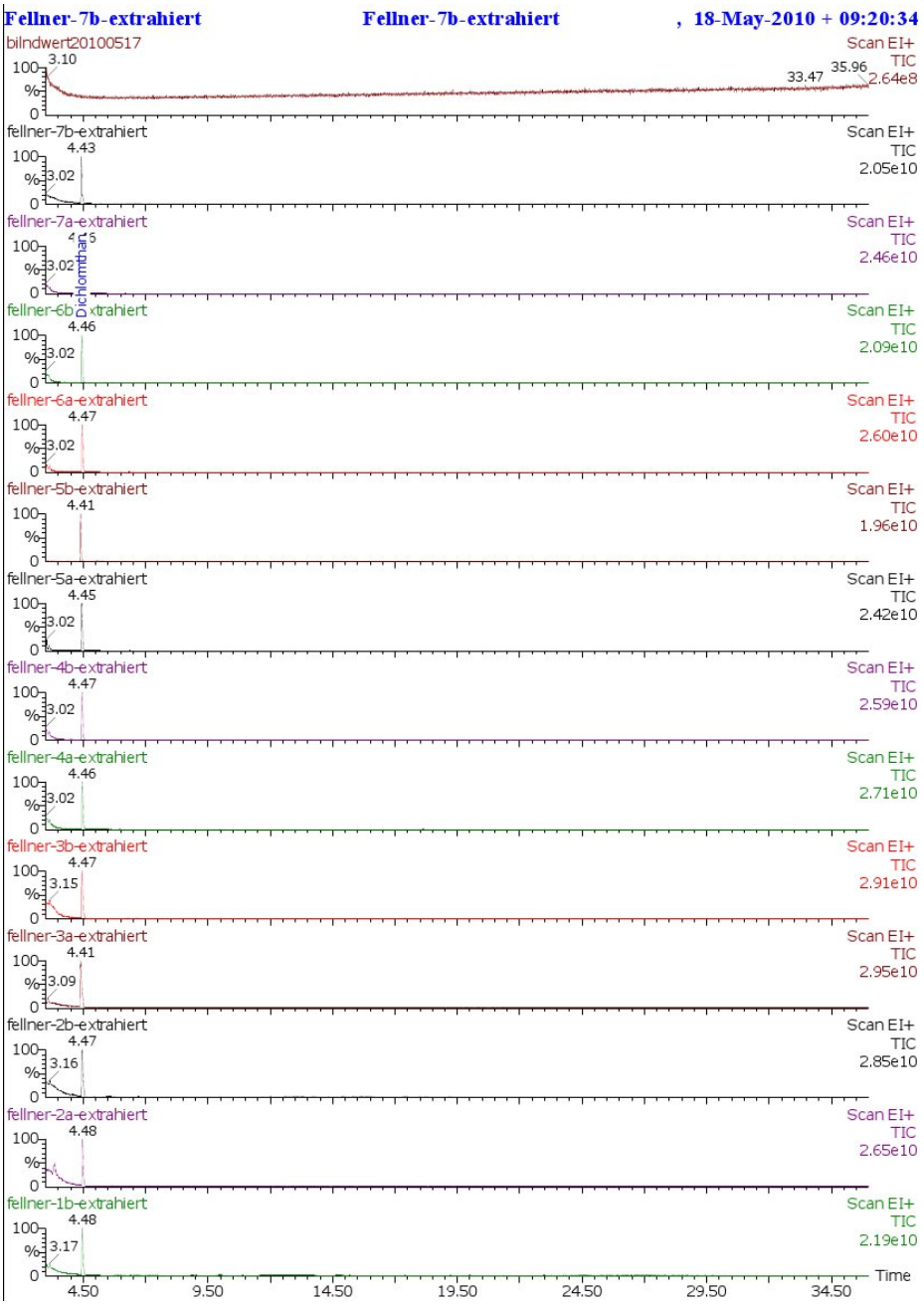

Figure 21: Sample 1 to 7 (with repeated series, except Nr. 1) and the blank

The unenhanced chromatograms are empty again, the only large peak is show at 4,48 it could be determent as the peak of dichloromethane which was the extracting agent for the Accelerated Solvent Extraction, so it is no surprise that this peak is present.

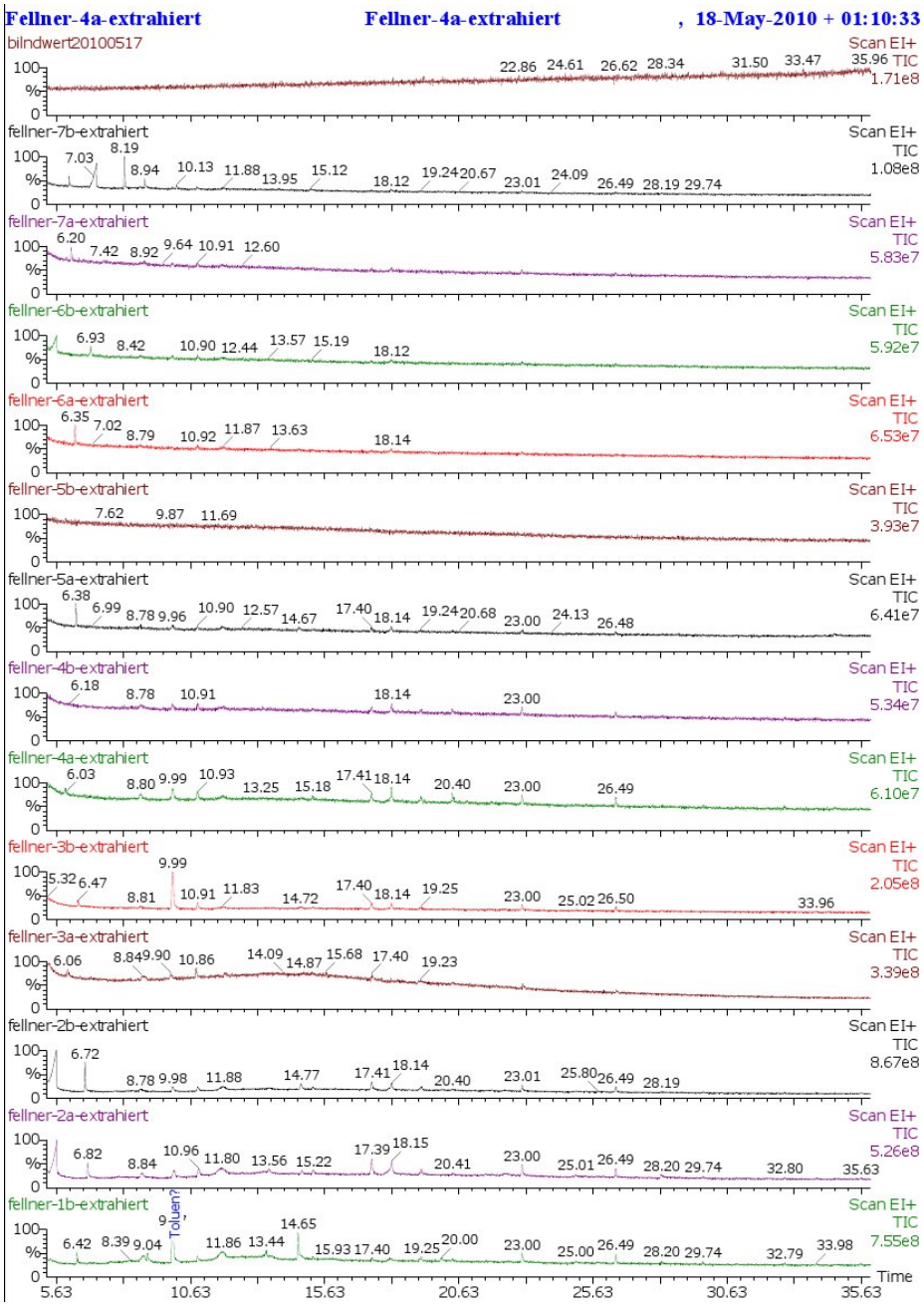

Figure 22: Enhancement after the 5. minute for sample 1 to 7 (with repeated series, except Nr. 1) and the blank

Again no real intensive peaks could be found, the 23,00 peak is still present but maybe even lower. The comparison is hard because all peaks are on such a small level in all chromatograms that the filter was empty before the extraction as the results of 4.10.1 show. And the extraction did not change anything there (except the expected peak of dichloromethane).

4.10.3 Results of the additional tests

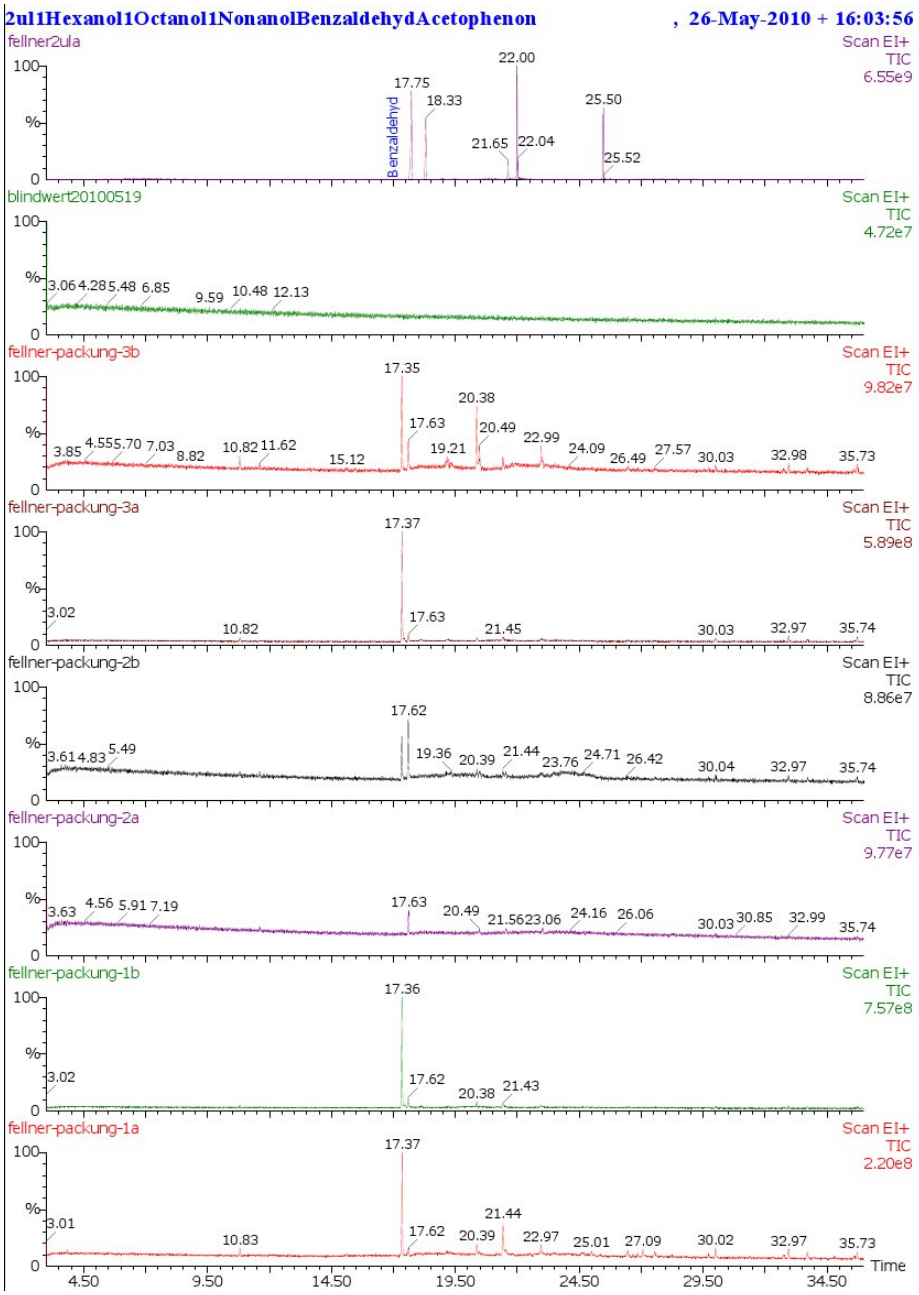

Figure 23: Enhancement after the 3. minute for the packaging of sample 1 to 3 (with repeated series), the blank and one chromatogram of the standards

The chromatogram was enhanced after the 3. minute to show the relevant peaks in greater detail, with the help of the library many peaks could be identified, so some standards were tested to compare the chromatograms (3 vials were prepared for that but all resulted in the same chromatogram, so only one is included here):

- The most intensive peak at the packaging of sample Nr. 1 and 3 is shown at **17,37** minutes, with the library it could be determent that the peak at **17,62** at Nr. 1 to 3 is the same substance: **benzaldehyde**
- The standard chromatogram confirmed this substance found with the library. It is most likely coming from the paint used on the outside of the packages
- Another peak that could be confirmed is shown at around **21,44**. The library and the standard comparison lead to **acetophenone**, most likely again coming from the printer's ink.

- Other peaks could not be identified as good but it is suspected that shorter alcoholic substances like heptanol or a similar branched substance is present too.

In the following illustration the standard chromatogram is shown with the labelling of the used standard substances:

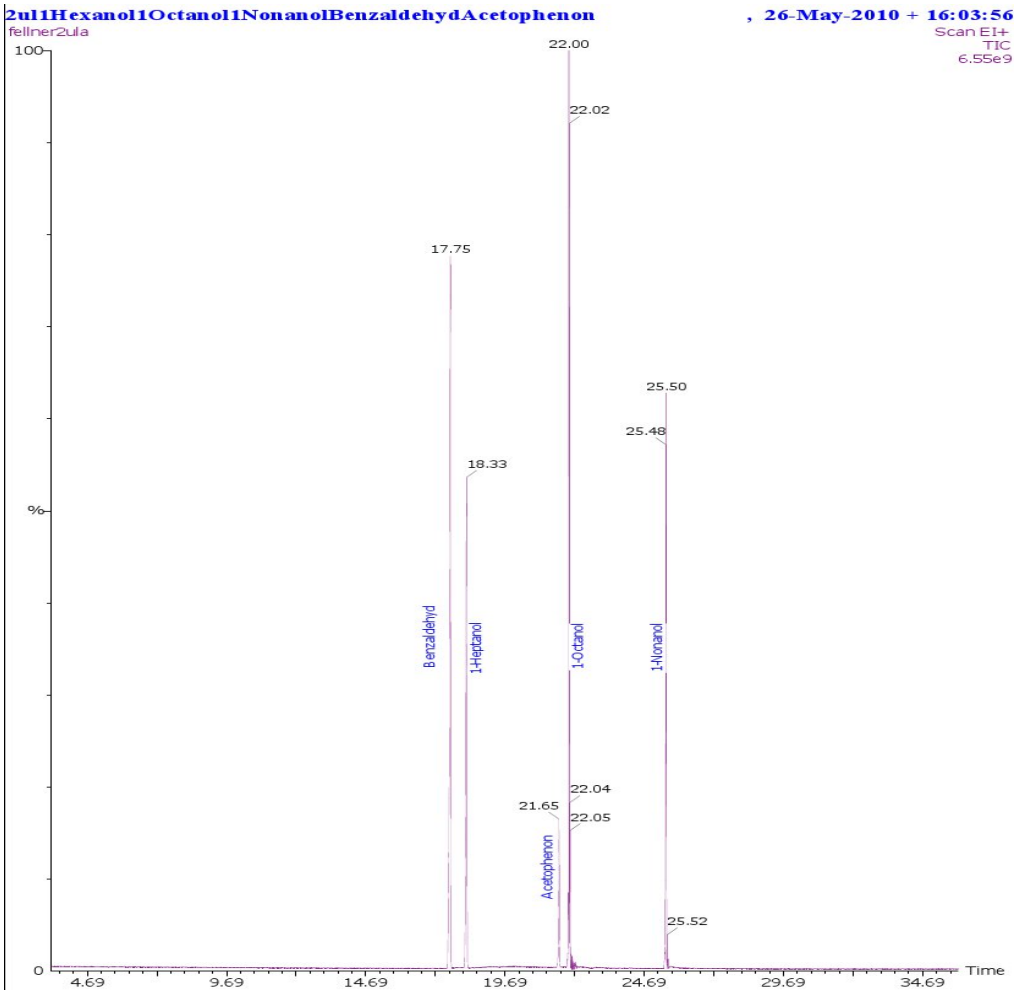

Figure 24: Enhancement after the 4. minute the standards with labelling

In **conclusion** this test-series proved that no substances are migrating from the packaging to the filters because neither benzaldehyde nor acetophenone were present in the filter chromatograms. The experiment also suggests that the packages themselves also are not containing any recycling material.

The advantage of this method was that no sample preparation is necessary and the results were available within hours. Qualification of the resulting peaks was possible to some degree with the internal library and with standards.
Quantification would also have been possible with standards for example but needs a lot more work to get to accurate numbers and since the samples showed no intensive peaks the quantification was not tried.

4.11 Results of the X-ray fluorescence spectroscopy

4.11.1 Spectra results

49 elements were tested simultaneously with 3 different targets which resulted in a lot of data material. The following images show the spectra based on those targets:

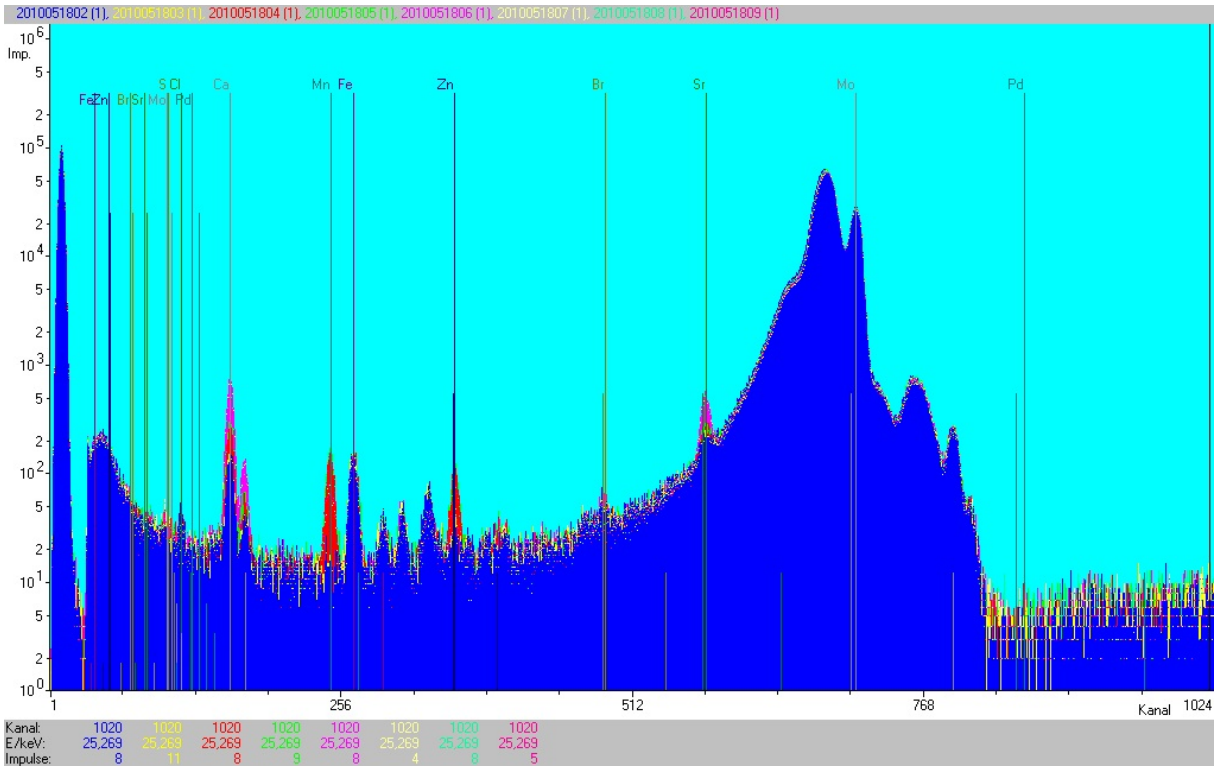

Figure 25: Spectra of the molybdenum target

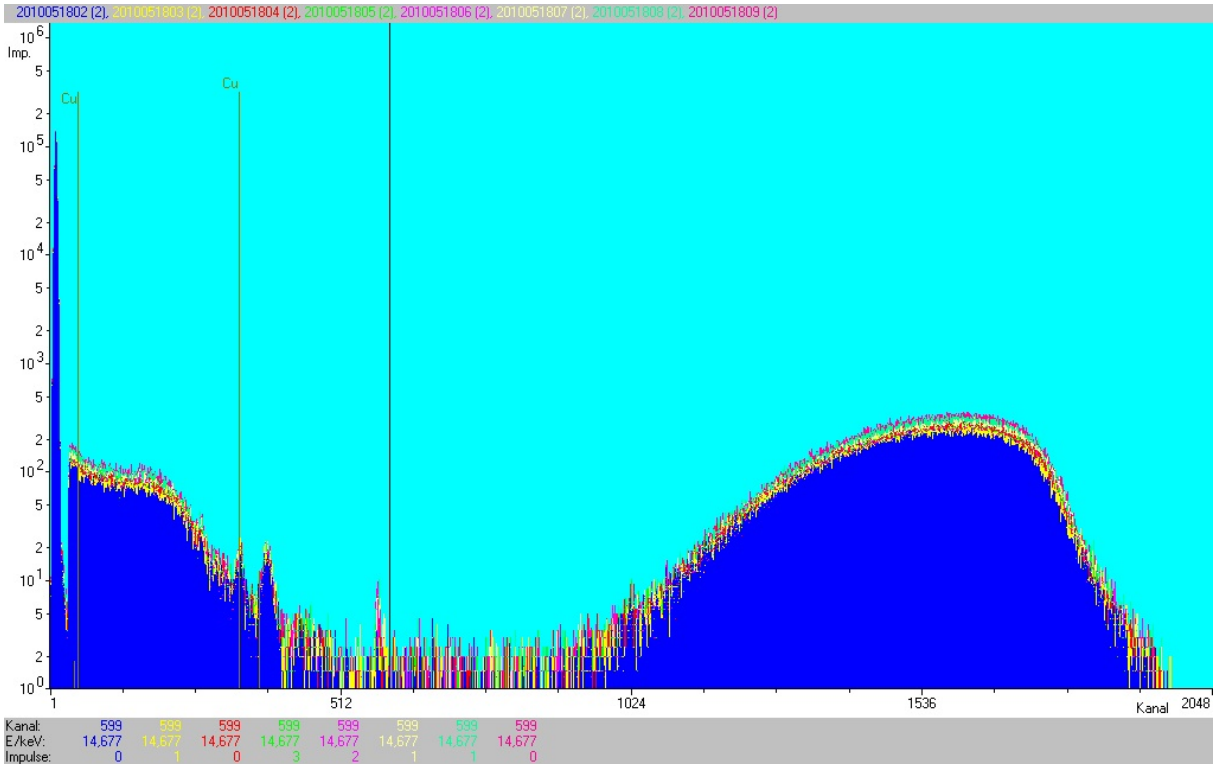

Figure 26: Spectra of the corundum target

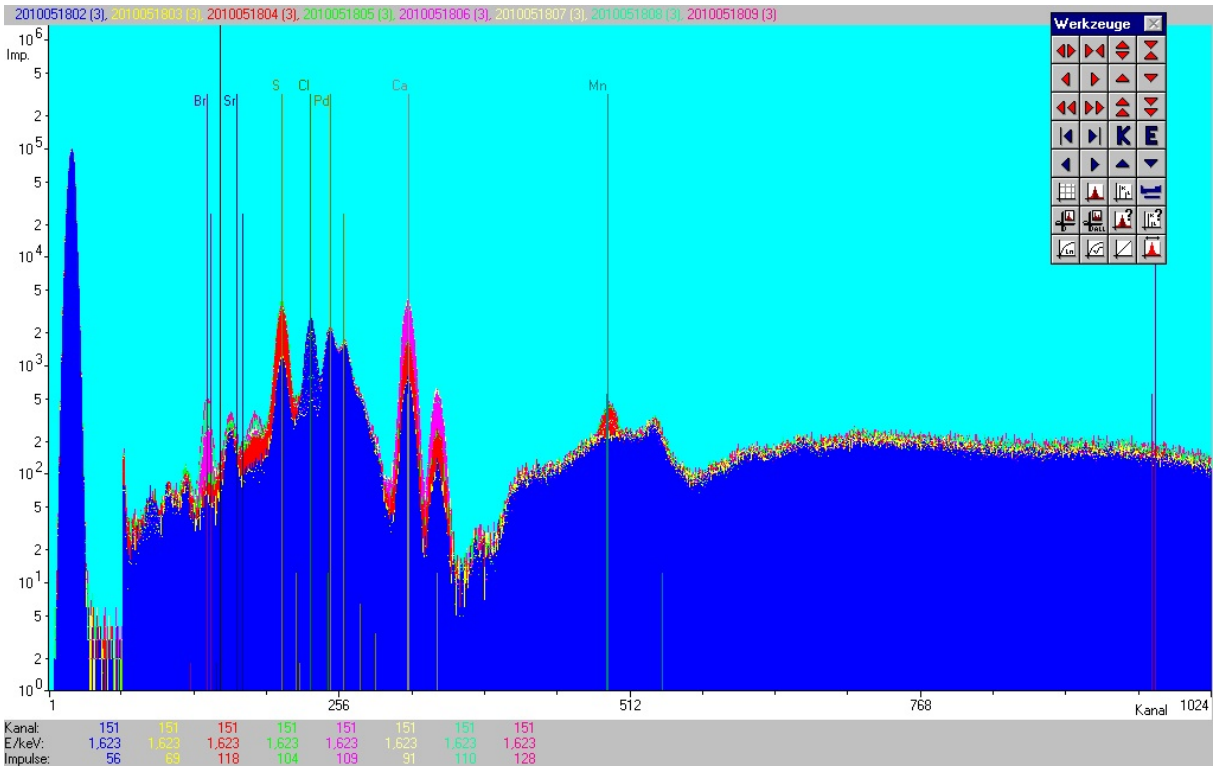

Figure 27: Spectra of the highly oriented pyrolytic graphite target

The spectra look different; other elements were measured with greater detail at each target. To come to a conclusion based on the graphical information was not needed; the software of the spectrometer combines the information of all targets and can give a % result of each element based on the 1g that was used for the test.

4.11.2 Results of the samples

In the following charts the average values of the percentage of the two test-series for the samples are shown:

Table 43: Elemental percentages of the samples Na-Cl

Sample	Na [%]	Mg [%]	Al [%]	Si [%]	S [%]	Cl [%]
1	0,13	0,04	0,02	0,04	0,05	0,05
2	0,12	0,07	0,02	0,04	0,18	0,03
3	0,08	0,06	0,10	0,03	0,18	0,01
4	0,05	0,04	0,13	0,03	0,11	0,01
5	0,15	0,10	0,03	0,05	0,26	0,05
6	0,08	0,07	0,02	0,03	0,15	0,02
7	0,17	0,10	0,03	0,05	0,24	0,07

Table 44: Elemental percentages of the samples K-Sr

Sample	K [%]	Ca [%]	Cr [%]	Mn [%]	Fe [%]	Cu [%]	Sr [%]
1	0,02	0,10	0,0004	0,0001	0,0057	0,0007	0,0003
2	0,02	0,20	0,0007	0,0069	0,0051	0,0004	0,0004
3	0,02	0,51	0,0004	0,0034	0,0047	0,0003	0,0010
4	0,01	0,27	0,0003	0,0055	0,0033	0,0002	0,0009
5	0,04	0,31	0,0006	0,0049	0,0055	0,0006	0,0005
6	0,02	0,20	0,0004	0,0054	0,0044	0,0003	0,0005
7	0,04	0,32	0,0003	0,0059	0,0064	0,0005	0,0005

All the other elements resulted in even lower % and are maybe not even present at all; some were shown to be under the detection limit, some were close to it.

Not shown are: P, Ti, V, Co, Ni, Zn, Ga, Ge, As, Se, Br, Rb, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, U

The % results are also not totally accurate because different limitations resulting were present. The method was not calibrated with paper standards similar to the filter paper but with other papers. The method was approved so it was used again, but the % are only giving a general direction and not totally accurate numbers!

4.11.3 Results of the sample packages

The same elements were shown again for the packages:

Table 45: Elemental percentages of the packages Na-Cl

Sample	Na [%]	Mg [%]	Al [%]	Si [%]	S [%]	Cl [%]
1P	0,14	0,13	0,80	1,47	0,13	0,04
2P	0,74	0,26	4,05	5,83	0,36	0,02
3P	0,23	0,21	3,70	4,27	0,35	0,03
4P	0,20	0,22	3,41	3,83	0,36	0,03
5P	0,32	0,19	3,12	4,78	0,31	0,07
6P	0,40	0,23	1,88	2,86	0,18	0,05
7P	0,27	0,10	1,14	1,60	0,15	0,02

Table 46: Elemental percentages of the packages K-Sr

Sample	K [%]	Ca [%]	Cr [%]	Mn [%]	Fe [%]	Cu [%]	Sr [%]
1P	0,14	12,85	0,0020	0,0058	0,1279	0,0059	0,0129
2P	0,01	21,51	0,0018	0,0053	0,1475	0,0216	0,0161
3P	0,18	12,16	0,0020	0,0051	0,1534	0,0091	0,0099
4P	0,16	11,79	0,0025	0,0047	0,1454	0,0056	0,0104
5P	0,03	23,59	0,0025	0,0060	0,1321	0,0159	0,0142
6P	0,02	13,85	0,0012	0,0034	0,0856	0,0049	0,0153
7P	0,01	7,98	0,0010	0,0020	0,0516	0,0056	0,0118

The other elements sometimes resulted in higher percentages at the packages than at the filter papers but the most common elements are still shown here.

4.11.4 Discussion of the results

The **error** of the experiment was already explained. The focus was not to get totally accurate percentages but an overview of the disposition of the elements. So an approved method with three different targets was used.
It is also important to notice that the main elements of the filter papers carbon, hydrogen or oxygen could not be measured with this method

So the **conclusions** are based on this overview and not the exact percentages:

- All samples showed no high concentrations of metals.

- At the **samples** the elements Na, S, Cl and Ca showed the highest percentages reaching ~0,1-0,3%. Sadly even those results might not be accurate because these elements are very light and at so small percentages the error of the method is relatively high. Those elements could also be contaminations from storage or from touching them with the bare hands, contaminations with NaCl for example are likely.
- The **packages** showed different numbers:
  - Fe, Cu or Sr range from ~0,01-0,1%
  - Al ~1-4%
  - Si ~1-5%
- Those metals are most likely coming from the printers ink on the packages.
- The highest concentration is shown at Ca. Which is also not surprising because $CaCO_3$ (chalk) is used as a filler material for cardboard like the packages.
- Because there is such a big difference between the relevant percentages of the filter papers and the packages, **migration of any metals is not likely**.
- Because the number of the metals is so low overall, it is also most likely that **no recycling paper was used** either at the filter papers or at the package.
- There was also **no indication of any toxic metals** like Hg, Cd, Chrome(VI) or Pb

4.12 Results of the Gas Chromatography Multimethod – Mass Spectrometry

The normal migration-stimulant for coffee brewing was water in the previous experiments but the multimethod is based on the extraction with dichloromethane. Which this extracting agent even more substances are extracted from the paper. So if concentrations are found here, the migrating equivalent of water would be much lower but maybe also occurring.

4.12.1 Results of the determination of Phthalates

There are many different phthalates and with the help of the internal standard DBP and DEHP they all can be measured and quantificated at the same time. The mass spectrometer detected the concentration of the standard and compared it to the signals of the different possible phthalates. The blanks were also tested and their result is subtracted from the sample-results.

In the following table the phthalate substances are listed which appear to be not present in the sample material since their signals were under the different detection limits:

Table 47: Results for all samples of the negative phthalates results

Substance	Concentration in the material [ng/g]
Dimethylphthalate	under the detection limit (=150 ng/g)
Diethylphthalate	under the detection limit (=200 ng/g)
Diallylphthalate	under the detection limit (=500 ng/g)
Dipropylphthalate	under the detection limit (=200 ng/g)
Benzylbutylphthalate	under the detection limit (=500 ng/g)
Dicyclohexylphthalate	under the detection limit (=800 ng/g)
Diphenylphthalate	under the detection limit (=800 ng/g)
Diisooctylphtalate (DIoP)	under the detection limit (=1000 ng/g)
Diisononylphtalate (DInP)	under the detection limit (=1000 ng/g)
Diisodecylphtalate (DIdP)	under the detection limit (=1000 ng/g)
Dioctylphthalate (DOP)	under the detection limit (=200 ng/g)

These are the more uncommon phthalates, so that no amounts were found is not that surprising.

At the next four charts the results of the more common phthalates are listed, were sometimes concentrations higher than the detection limits (dl) were found, since concentrations under those limits are not reliable, they are also not included in the average value:

Table 48: Results for Diisobutylphthalate (DIBP - Detection limit 200ng/g / 0,2mg/kg)

Sample	concentration 1. test-series [ng/g]	concentration 2. test-series [ng/g]	average value concentration [mg/kg]
1	2102,4	2845,4	2,47
2	3500,6	3278,4	3,39
3	1709,9	822,6	1,27
4	2874,2	3180,6	3,03
5	1667,9	2475,6	2,07
6	2381,3	2855,7	2,62
7	927,5	816,7	0,87

Table 49: Results for Dibutylphthalate (DBP - Detection limit 400ng/g / 0,4mg/kg))

Sample	concentration 1. test-series [ng/g]	concentration 2. test-series [ng/g]	average value concentration [mg/kg]
1	686,5	586,9	0,69
2	542,8	under the dl (129,9)	0,54 / under the dl
3	534,6	under the dl (140,5)	0,53 / under the dl
4	886,1	under the dl (247,9)	0,89 / under the dl
5	682,2	795,8	0,68
6	801,0	615,2	0,80
7	under the dl (53,5)	under the dl (19)	under the dl

Table 50: Results for Diethylhexyladipate (DEHA - Detection limit 500ng/g / 0,5mg/kg)

Sample	concentration 1. test-series [ng/g]	concentration 2. test-series [ng/g]	average value concentration [mg/kg]
1	under the dl (462,6)	under the dl (329,0)	under the dl
2	under the dl (178,1)	under the dl (229,7)	under the dl
3	5828,3	under the dl (99,9)	5,83 / under the dl
4	2111,8	649,7	1,38
5	3908,2	1733,1	2,82
6	725,4	under the dl (277,3)	0,73 / under the dl
7	under the dl (146,3)	under the dl (33,4)	under the dl

Table 51: Results for Diethylhexylphthalate (DEHP - Detection limit 400ng/g / 0,4mg/kg)

Sample	concentration 1. test-series [ng/g]	concentration 2. test-series [ng/g]	average value concentration [mg/kg]
1	1422,0	878,0	1,15
2	471,2	799,1	0,64
3	4538,2	628,0	2,58
4	4599,6	1973,8	3,29
5	4045,5	867,9	2,46
6	627,2	453,0	0,54
7	478,4	560,2	0,52

4.12.1.1 General discussion of the results

The blanks were not listed here. Their result was good because all concentrations were lower than the detection limits at all substances and their numbers is already factored in the shown results.

That the uncommon phthalates were under the detection limits is a good result for the filter paper, it also proves that most likely nothing went wrong at the lab work.

The more common phthalates can be found in almost every consumer product, so it is no surprise that some concentrations could also be found at this experiment in the filter papers at those extreme extracting conditions with dichloromethane, pressure and temperature.

At the safety limits of the following phthalates (48) it is important to note that these safety limits are for food simulates most common water for coffee.

There are no safety limits for the extreme extraction conditions which were applied, so in general it save to say that the concentrations would be much lower in a water-extract or in coffee.

4.12.1.1.1 Results for Diisobutylphthalate

At **Diisobutylphthalate** (DIBP) the concentrations were notably higher than the detection limit. Between the two test-series the variations were not that high, an average value of the two results gives a good general picture of the DIBP content in the filter papers.
The concentrations in the dichloromethane-extract are higher than the safety limit of 1mg/kg for a water-extract.

In the following picture the results for DIBP are summarized:

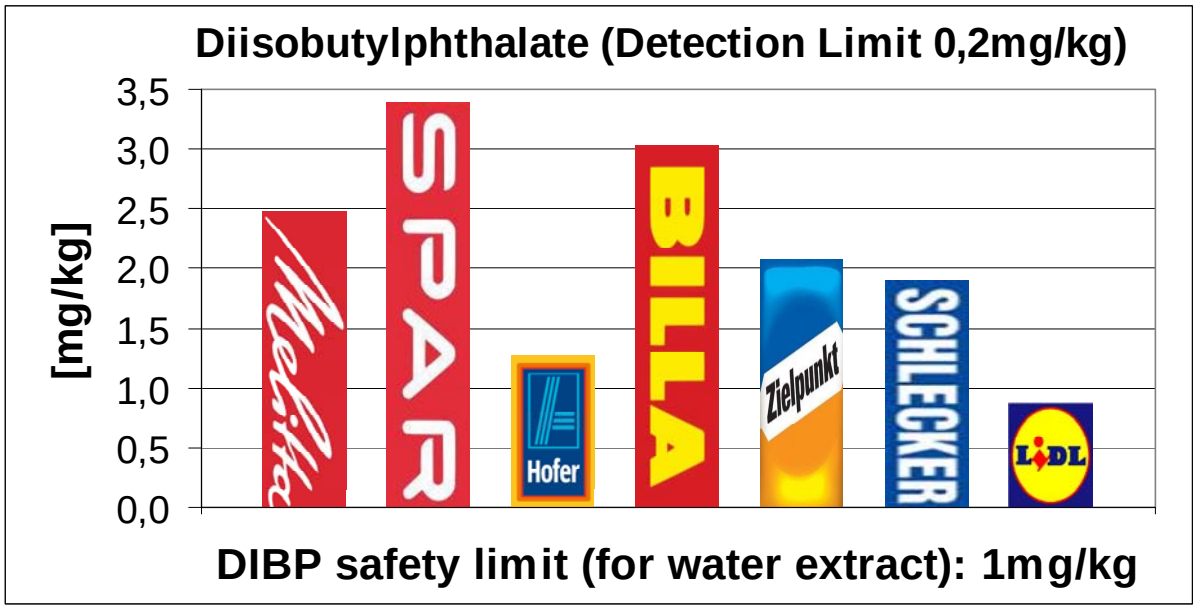

Figure 28: Results for Diisobutylphthalate for samples 1-7

An average of two test-series might not be that reliable but the concentrations at DIBP don't fluctuate that much. So the following **conclusions** can be drawn concerning the differences between the samples which are portable to a food stimulant or coffee:

- Here sample Nr. 2 and 4 show the highest concentrations.
- Sample Nr. 5 and specially Nr. 1 and Nr. 6 do not stand out as they did in previous tests.
- Sample Nr. 3 and 7 show the lowest concentration, again the best result at the samples for sample Nr. 7. Its concentration is under the safety limit (48) even under the applied conditions.
- In the end all concentrations are so close to the detection limit for a water-extract, that there is no real reason for concern.

4.12.1.1.2 Results for Dibutylphthalate

The concentration results of **Dibutylphthalate** (DBP) are a little bit more fluctuating between the two test-series. Most concentrations are close to the detection limit and some are even under it, so sometimes no average value could be determent (at sample Nr. 2, 3 and 4) and only one concentration was factored into the following figure:

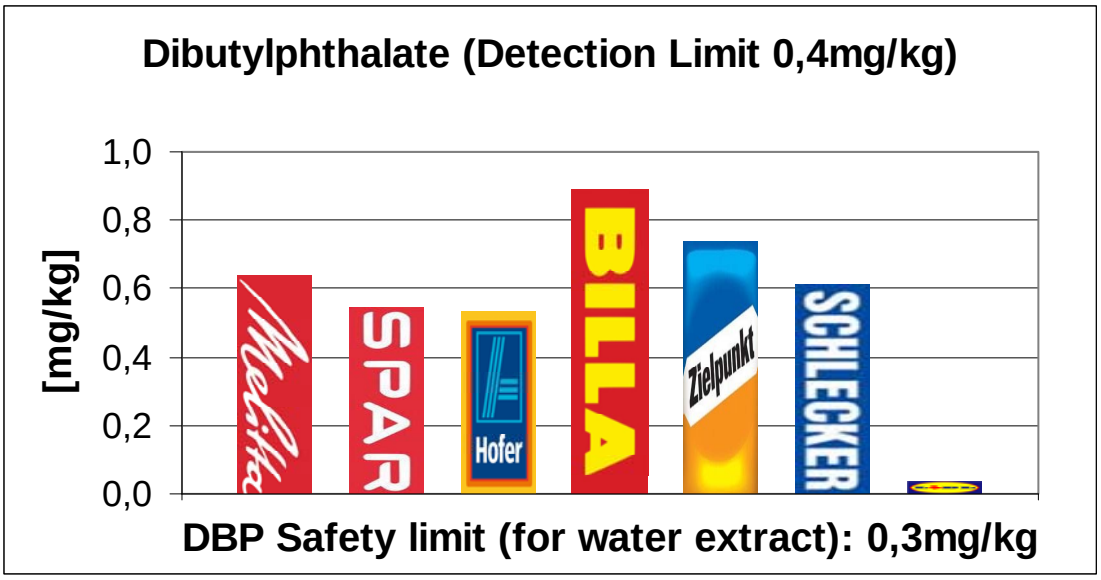

Figure 29: Results for Dibutylphthalate for samples 1-7

Sample Nr. 7 showed two results under the detection limit. The safety limit for this substance in a water-extract is even lower than the detection limit of the used mass spectrometer.

Again the following conclusions are possible focusing on the differences between the samples:

- Again the concentrations are close to the safety limit (48) or in this case close to the detection limit.
- The concentrations are not that reliable, for example sample Nr. 4 showed the highest concentration one time and at the second series it was under the detection limit. Reasons could be the difference between the samples inside one package. On the outside the phthalate concentration could be a little higher. Contaminations from the lab work are not likely but possible.
- Sample Nr. 7 showed two results under the detection limit, again the best result of all samples.

- But again all concentrations in this extreme extract were so low, that there is not much to worry about.

4.12.1.1.3 Results for Diethylhexyladipate

The results of **Diethylhexyladipate (DEHA)** showed little strange results. Out of the 14 concentrations (7 samples with one repeated series) 10 were under or close to the detection limit. But 4 concentrations were four to ten times higher than the detection limit; these occurred at sample Nr. 3, 4 and 5. It is hard to get to a conclusion at this substance; in the following graphically summary also the numbers under the detection limit were included maybe to give a better comparison:

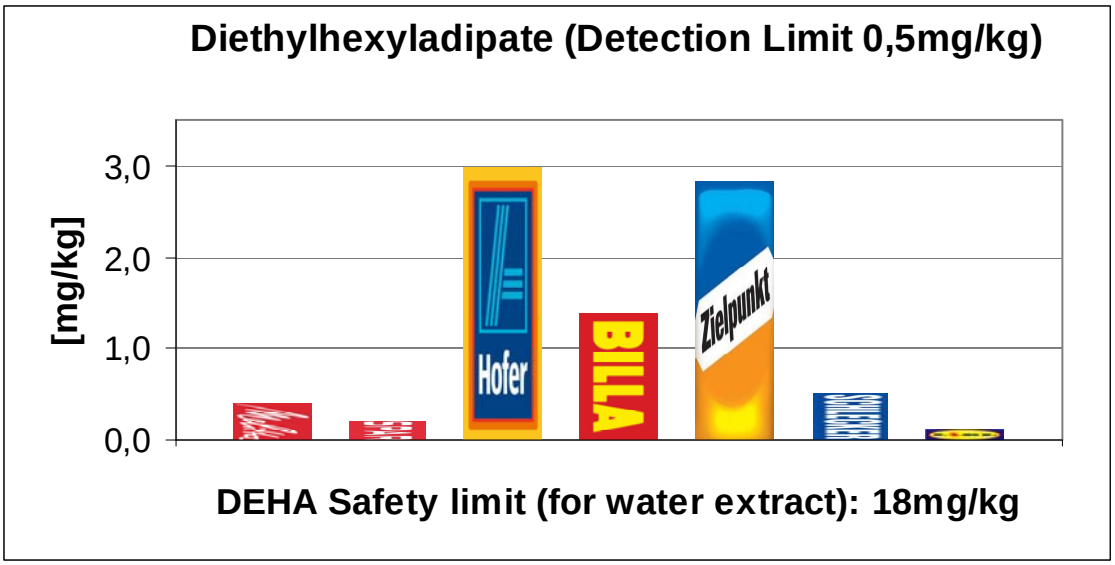

Figure 30: Results for Diethylhexyladiapate for samples 1-7

The possible errors are the same as mentioned at DBP; here the 4 high results really make it hard to say which results are accurate. The figure shows the average value and so the concentrations of sample Nr. 3, 4 and 5 are a little lower. For example sample Nr. 3 showed a result of nearly 6mg/kg at one series and then 0,1mg/kg at the other.

In **conclusion** it seems that even something went a little wrong at the lab-work or the measurement or maybe there are high fluctuations at DEHA at the filter papers.

- Sample Nr. 3, 4 and 5 seem to have a high amount at DEHA, at least at some samples, in this case at the random chosen first test-series.
- Again sample Nr. 7 showed really low concentrations, since both test-series lied under the detection limit it is most likely that there was no DEHA present in the sample. This could also be the case at sample Nr. 1, 2 or 6.
- The safety limit of DEHA (48) is much higher than at the other phthalates, so even the 4 high numbers are not that concerning.

4.12.1.1.4 Results for Diethylhexylphthalate

Nearly the same problems with the results occurred at **Diethylhexylphthalate** (DEHP) because again sometimes the two test-series showed no reproducible results. But here all results were over the detection limit.
Under the 14 results, there are 4 or 5 really high concentrations compared to the remaining. Especially the first result of sample Nr. 3, 4 and 5 were higher than the rest again like at DEHA. This is actually a good thing since the reason lies most likely at the sample. Again the average values are shown in an illustration:

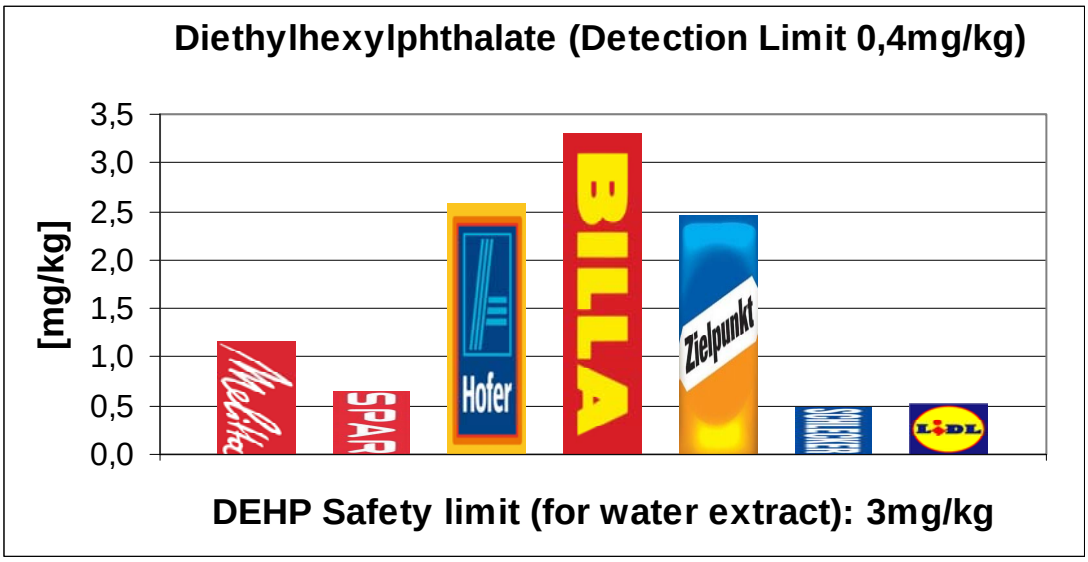

Figure 31: Results for Diethylhexylphthalate for samples 1-7

As said above, the 3 samples of the first test-series at Nr. 3, 4 and 5 stick out again.

In **conclusion** the result of DEHP approves the results of DEHA, at 3 samples out of the 14 the concentrations of the phthalates seem to be higher.

4.12.2 Results of the determination of pentachlorophenol

The concentrations for the different substituted chlorophenols were all determent with recovery rate the internal 13C Pentachlorophenol standard, except the Polychlorinated Biphenyl which used its own standard.

In the next chart the results for analysed substances for all samples are shown:

Table 52: Results for all samples of the chlorophenol determination

Substance	Concentration in the material [ng/g]
2-Chlorophenol	under the detection limit (=50 ng/g)
3-Chlorophenol	under the detection limit (=50 ng/g)
4-Chlorophenol	under the detection limit (=50 ng/g)
2,3-Dichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,4-Dichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,5-Dichlorophenol (derivatized)	under the detection limit (=50 ng/g)
3,5-Dichlorophenol (derivatized)	under the detection limit (=50 ng/g)
3,4-Dichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,3,5-Trichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,4,5-Trichlorophenol (derivatized)	under the detection limit (=50 ng/g)

2,4,6-Trichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,3,4-Trichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,3,6-Trichlorophenol (derivatized)	under the detection limit (=50 ng/g)
3,4,5-Trichlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,3,5,6-Tetrachlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,3,4,5-Tetrachlorophenol (derivatized)	under the detection limit (=50 ng/g)
2,3,4,6-Tetrachlorophenol (derivatized)	under the detection limit (=50 ng/g)
Pentachlorophenol (derivatized)	under the detection limit (=50 ng/g)
13C6-Pentachlorophenol	under the detection limit (=50 ng/g)
Polychlorinated Biphenyl	under the detection limit (=50 ng/g)

In **conclusion** all samples were negative for all kinds of chlorophenols which is also a good result compared with the failed photometric approach. All substances show no concentrations at all or were under the detection limit of the mass spectrometer of 50ng/g.

That no concentrations could be found is also not surprising since pentachlorophenol is forbidden to be used at paper products in the European Union for over a decade.

4.12.3 Results of the determination of benzophenone

4.12.4 Results of the determination of diisopropylnaphthalene

4.12.5 Results of the determination of Michler's ketone

4.13 Results of the determination of Dioxins

4.14 Results of the Determination of perfluorinated compounds

4.15 Results of the Gas Chromatography Echelle Plasma Emissions Detector

In the following table the amount of the total fluorine content is listed and also the fraction of **fluorotelomer alcohol** (FTOH), **fluorotelomerthiol** (FTSH) and the resulting unknown content.

Table 53: Results of EPED measurements for fluorinated c substances

Sample	Total area (ng F/dm²)	FTOH (ng F/dm²)	FTSH (ng F/dm²)	unknown (ng F/dm²)
1	3,47	2	0	2
2	2,81	0	0	2
3	2,90	0	0	2
4	3,67	0	0	3
5	1,96	1	0	1
6	0,19	0	0	0
7	0,15	0	0	0

The concentrations shown are not really low and are not real concentrations but the included noise of the blanks. So no fluorinated substances are present at the filter papers.

5 CONCLUSION

In the **first part** of the Diploma work the focus lied on getting as much general information on the filter paper samples.

From the informations on the packages and the **optical impressions** of the filters not many differences could be found, only the one bleached filter (sample Nr. 1) stuck out a little with its white colour. The **contact area** is very similar because the samples are of the same standardized size 4.
The **weight** is also similar but differences could be worked out, the bleached filter seems to be the heaviest by a small margin.
The **moisture content** is also nearly the same for all filters, with around 0,5-1% it is relative low for a commercial paper product but this could also be a result of conditions when the tests were performed or the storage of the samples until the experiments.

The pictures from the **scanning electron microscope** only compared sample Nr. 1 and 4 but since no visible contaminations could be determent, it is most likely that the other samples had none too.

Then the first more basic tests of the **coldwater** and **hotwater extracts** followed.
The **dry matter content of the coldwater extracts** of the bleached filter was twice as high at ~5000mg/kg compared to the other samples which ranged from ~1500 to 2300mg/kg.
The **dry matter content of the hotwater extracts** was similar at most samples, only the bleached filter was much lower (but still the highest with ~2700mg/kg).
So the extractions methods seem to extract about the same amount, maybe the hotwater output is a little higher in general. The bleached filter (sample Nr. 1) sticks out with the highest numbers, sample Nr. 4 with the lowest.

The **pH** rose for about 0,5 compared to the blank at all samples and at both extracting methods. The small differences seem to be within the margin of error. So the migrating substances have an influence on the pH of the extract but only a small one.

With the **Potassium permanganate method** the organic content was determent. Only one test-series was performed and the experiment also did not result in very exact amounts but a general overview was possible at the none volatile organic substances. Again sample Nr. 1 resulted in the highest amount with ~6mg/dm², followed with ~4mg/dm² at sample Nr. 2 and 7. The other four samples all resulted in ~2,5mg/dm².

So all these first experiments made the impression, that the filters were all very similar concerning these general parameters, only the bleached filter stacked out a little.

In the **second part** of the Diploma work it was tried to determent the amount of certain migrating substances and maybe also to find out if other harmful chemicals are present.

The **photometric measurements** of **glyoxal** and **formaldehyde** resulted both in rather low concentrations, much lower than the safety limits. Between the samples the amounts were very similar at both substances and at both extracting methods. The sequence of the concentrations is summarized here:

Glyoxal coldwater extracts: 6 > 2 > 5 > 7 > 3 > 1 > 4

Glyoxal hotwater extracts: 6 > 3 > 4 > 5 > 1 > 2 > 7

Formaldehyde coldwater extracts: 6 > 2 > 4 > 5 > 7 > 1 > 3
Formaldehyde hotwater extracts: 6 > 3 > 4 > 5 > 1 > 2 > 7

The coldwater extracts are very similar, the hotwater sequence is identical. Sample Nr. 6 seems to have the highest amounts, sample Nr. 1 and 7 the lowest. But again all the samples resulted in very low unconcerning amounts.

Sadly the **photometric measurements** of **pentachlorophenol** in the coldwater extracts did not work as hoped.

Gas chromatography-Mass Spectrometry analyses of **pentachlorophenol** and similar chlorinated phenols showed that no amounts of those substances were present in the dichloromethane extracts at all samples.

Gas chromatography-Mass Spectrometry analyses of the different **phthalates** in the dichloromethane extracts also showed no concentrations at the more uncommon ones.

At **Diisobutylphthalate** (DIBP), **Dibutylphthalate** (DBP), **Diethylhexyladiapate** (DEHA) and **Diethylhexylphthalate** (DEHP) detectable amounts were present at nearly all samples. Sadly some results were not repeatable by the second performed test-series. Overall all results in the dichloromethane extracts were always close over or under the safety limits for the substances in water extracts. So most likely the amounts in a water extracts would have been under the detection limit of the Mass Spectrometer.
Sample Nr. 3, 4 and 5 mostly had the highest amounts; sample Nr. 7 was notably lower than all the other samples at all substances.

The EPED measurements showed that no fluorinated substances were present in detail no **perfluorinated compounds** like **fluorotelomer alcohol** (FTOH) or **fluorotelomerthiol** (FTSH).

The **Headspace-Gas chromatography-Mass Spectrometry** method showed that no high amounts of any vaporable substances until 150°C were present in the samples which could later migrate. There were some unsolved peaks present but these were very tiny and tolerable. This method also settled the impression that no recycled paper was used either for the filter papers or for the packages and that no large migration took place from the packages to the filter papers. Some substances from the packages most likely from the printers ink were not found at the filter papers.

Lastly the **X-Ray fluorescence spectroscopy** also established these results because the higher metal amounts of the packages were not present in the filter papers. The filter papers were very clean concerning metals, most important no traces of toxic metals were present. And again no indications of recycled paper were found.

In **conclusion** all results show that the filter papers all seem to be safe and clean:

- **No big migration** seems to occur **between the packages and the filter papers**.
- **No recycled paper** is most likely used for the production of the packages or the filter papers, no substances suggesting anything else were found.
- **No safety limits are exceeded** at **glyoxal, formaldehyde** and **pentachlorophenol.**

- **No indication of toxic metals or high concentration at other metals (specially no higher chlorine levels point to no presence of dioxins)**
- **No indication of fluorinated substances (also a sign for no present dioxins)**
- **No indication of any other concerning substances**
- **No amounts of the uncommon phthalates** are present.
- **At the more common phthalates some amounts are detectable** under the extreme extracting conditions. These results are maybe the only one which cause a little concern but most likely the concentrations are nothing to worry about
- **An extraction of substances is defiantly happening**, these substances rise the pH by ~0,5 for example. But it seems that no migration of harmful substances is present and most likely no harmful substances are even present in the paper.

- **These conclusions are true for all 7 samples, all samples showed very good and unconcerning results overall**
- **The bleached sample Nr. 1** seems to have a higher amount of migrating substances but most likely safe ones like normal paper fibers
- **The unbleached samples Nr. 2, 3, 4, 5 and 6 are all very similar**, small differences could be worked out.
- **The unbleached sample Nr. 7** scored lowest at most concentrations at nearly all experiments, so the production of this product occurs to be the best

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