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# Interferences in the direct quantification of bisphenol S in paper by means of thermochemolysis

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ABSTRACT

This article analyses the interferences in the quantification of traces of bisphenol S in paper by applying the direct analytical method "analytical pyrolysis gas chromatography mass spectrometry" (Py-GC/MS) in conjunction with on-line derivatisation with tetramethylammonium hydroxide (TMAH). As the analytes are simultaneously analysed with the matrix, the interferences derive from the matrix. The investigated interferences are found in the analysis of paper samples, which include bisphenol S derivative compounds. As the free bisphenol S is the hydrolysis product of the bisphenol S derivative compounds, the detected amount of bisphenol S in the sample may be overestimated. It is found that the formation of free bisphenol S from the bisphenol S derivative compounds is enhanced in the presence of tetramethylammonium hydroxide (TMAH) under pyrolytic conditions. In order to avoid the formation of bisphenol S trimethylsulphonium hydroxide (TMSH) is introduced. Different parameters are optimised in the development of the quantification method with TMSH. The quantification method based on TMSH thermochemolysis has been validated in terms of reproducibility and accuracy.

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## 1. Introduction

Paper and its constituents are frequently evaluated regarding their health impacts, as frequent contact with paper is inevitable. It is therefore important to evaluate the concentration of compounds in paper that may be hazardous to human health such as 4,4′-dihydroxy-2,2′-diphenylpropane, usually known as bisphenol A (or BPA) [1–4].

During 2005/2006 the European production of bisphenol A amounted to approximately 1.15 million ton. About 0.2% of the produced amount was used for the production of thermal printer paper and carbonless paper [5]. Approximately 30% of the used thermal paper consumed enters recycling streams [6]. Although cleaning in the recycling process removes most impurities from the paper, some residues remain in the final product. Hence, bisphenol A can be found in recycling paper products.

During the last decades the potential impacts of bisphenol A on human health have frequently been debated [1–4]. However, to date, the existing studies about BPA and its health impacts remain inconclusive [7–11]. The controversy on the subject of bisphenol A involves various non-governmental and governmental assessment bodies [12]. In 2010 the U.S. Environmental Protection Agency (EPA) declared bisphenol A as a chemical of concern. In the same year the EPA initiated the Design for the Environment (DfE) programme to encourage, amongst others, the removal of bisphenol A from thermal printer paper and carbonless paper [13]. One of the programme's objectives is to find alternative compounds for bisphenol A.

In 2010 the EPA issued a list of functional chemical alternatives for bisphenol A [14], which includes the compound 4-hydroxyphenyl sulphone (bisphenol S or BPS) and its derivatives such as 4-hydroxyphenyl 4-isoprooxyphenylsulphon (or D8), 4-((4-(2-propen-1-yloxy)phenyl)sulphonyl)phenol (or BPS-MAE), and 4-(4′-((1′-methylethyloxy) phenyl)sulphonyl)phenol (or D90). Bisphenol S and its derivatives have not been investigated as widely as bisphenol A with regard to the impact on human health. Some assays on the impact of bisphenol S on human health report weaker estrogenic activity compared with bisphenol A [15,16].

The identification and quantification of bisphenol A are frequently examined issues [17,18]. However, regarding the quantification of bisphenol A, bisphenol S and their derivatives in paper samples, documentation is scarce. The determination of bisphenol A in paper samples usually combines various steps. The methods involve the extraction (isolation), concentration, and derivatisation of the analytes prior to analysis *via* GC or HPLC [19–22]. According to recent studies, the analytical pyrolysis GC/MS method [23] is found to be conclusive for the direct quantification of bisphenol A and bisphenol S in paper samples.

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Analytical pyrolysis combines the strengths of pyrolysis sample preparation with gas chromatographic product separation and mass spectrometric detection [24,25]. This powerful tool is commonly used for the direct characterisation of solid samples [26] such as many synthetic polymers but also of pulp, paper, and their additives [27–30].

The direct determination of analytes simplifies sample preparation and reduces the costs and time needed for the analysis. Furthermore, the possible measurement of very small quantities makes analytical pyrolysis interesting in terms of solving analytical tasks in compliance with the principles of green analytical chemistry [31,32]. Despite its advantages, analytical pyrolysis is considered as insufficiently reliable to meet the challenges of analytical chemistry [33]. The fact that analytical pyrolysis is more widely applied in solving qualitative rather than quantitative analytical tasks shows that its potentials are much underestimated.

Direct analytical methods are able to produce valid results and this holds true for analytical pyrolysis as well. However, the application of direct analytical methods may produce errors ensuing from the sample itself, also known as matrix effects. In analytical pyrolysis the matrix and other sample additives simultaneously undergo thermal cleavage at elevated temperatures in an oxygen-free atmosphere. Consequently, large numbers of compounds are present during the analysis, which might interfere in analyte identification and analyte quantification [34,35] affecting the selectivity of the analytical method.

Analytical pyrolysis combined with on-line derivatisation with TMAH, also known as TMAH thermochemolysis, harbours the risk of creating additional sources of errors. In TMAH thermochemolysis, the non-selective reaction of the derivatisation agent has been previously reported [36,37]. The lack of selectivity in the derivatisation with TMAH might render the specificity of the analytical method unreliable. Therefore, the development of a direct analysis method merits careful scrutiny in terms of selectivity and specificity.

This study serves to evaluate the interferences in analytical pyrolysis with TMAH on-line derivatisation of paper samples (or TMAH thermochemolysis). In order to reduce the interferences that occur from the thermochemolysis reaction and to enhance the specificity of the analytical method for the quantification of bisphenol S, trimethylsulphonium hydroxide (TMSH) is introduced as derivatisation reagent. The TMSH thermochemolysis parameters are optimised. The TMSH thermochemolysis analytical method is assessed in terms of reproducibility and accuracy. In addition, the TMSH thermochemolysis quantification method is compared with the TMAH thermochemolysis method previously validated [23].

## 2. Materials and methods

### 2.1. Materials and reagents

Bisphenol A (99%), bisphenol S (98%), tetramethylammonium hydroxide (TMAH, 25 wt.% in water) and trimethylsulphonium hydroxide (TMSH, 25 wt.% in methanol) are acquired from Sigma Aldrich. Bisphenol S derivatives (4-hydroxyphenyl 4-isoprooxyphenylsulphon (D8), 4-(4-(2-propen-1-yloxy)phenyl)sulphonyl)phenol (BPS-MAE), and 4-(4′-((1′-methylethyloxy) phenyl)sulphonyl)phenol (D90) (99%) from different producers are acquired through a thermal paper company. HPLC-grade acetone, analytical-grade methanol, and methyl *tert*-butyl ether (99%) are obtained from Merck (Darmstadt, Germany). Water is purified in a Purelab® Option-Q ELGA DV 25 system to conductivity levels below 0.5 μS/cm.

Various stock solutions of bisphenol A and bisphenol S are prepared by dissolving both compounds in acetone at different concentrations. Diluted solutions are required for the preparation of the calibration samples and prepared from the previous stock solutions. Each diluted solution is made from a different stock solution.

Hand sheets are produced from industrially manufactured fully bleached spruce acid sulphite pulp (SSP) in the laboratory of the Holz Wirtschaft Institut according to Zellcheming standard V/8/76. The SSP serves as a reference substrate.

Six industrially produced thermal papers, labelled as bisphenol A-free, two samples of recycled letter paper and copy paper with virgin fibres are used for the validation of the method.

### 2.2. Instrumentation

#### 2.2.1. Pyrolysis-GC/MS

The Py-GC/MS analysis is carried out in a Frontier Lab Micro furnace Double-shot Pyrolyzer (EGA/Py-3030iD) equipped with an autosampler (AS-1020 E). If not otherwise mentioned, the temperature for pyrolysis is set at 400 °C and the interface temperature at 360 °C with pyrolysis time of 0.5 s. Helium is used as carrier gas for the pyrolysis and the gas chromatographic separation. After the pyrolysis step, the pyrolysate is directly transferred into a DB5 fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) with a split ratio of 30:1.

For gas chromatographic separation the flow rate is 1 ml/min. The temperature of the oven programme of the gas chromatograph starts at 100 °C, with increments of 10 °C/min immediately up to 250 °C. Once the temperature reaches 250 °C, the heating rate changes to 5 °C/min until reaching 275 °C. Once the temperature reaches 275 °C the heating rate changes to 15 °C/min until 320 °C. This temperature is kept for 5 min. For mass spectral detection a 5973 N agilent inert MS using 70 eV electron impact ionisation energy is applied. The scan range for the measurement in total ion modus is 35–400 *m*/*z*. The selective ion mode (SIM) of the mass spectrometer is applied for the quantification of bisphenol A and bisphenol S. Two mass fragments for each compound (*m*/*z* 256 and 241 for bisphenol A and *m*/*z* 278 and 123 for bisphenol S) are selected.

#### 2.2.2. GC/MS

The GC/MS analyses are performed with a G1530A agilent gas chromatograph equipped with a Combi PAL autosampler.

For gas chromatographic separation the flow rate is 1.9 ml/min. The temperature of the oven programme of the gas chromatograph starts at 100 °C with increments of 15 °C/min immediately up to 320 °C. This temperature is kept for 5 min. For mass spectral detection a MS 5972A is used. The selective ion mode (SIM) of the mass spectrometer is applied for the quantification of bisphenol S with three mass fragments (*m*/*z* 123, 155, and 278).

### 2.3. Sample preparation

The sample preparation for analytical pyrolysis consists in placing small sample pieces of 120 ± 5 μg into the sample cups and adding 10 μl of the derivatisation reagent TMSH (10 wt.% in methanol/water).

For calibration samples preparation, a piece from a paper sheet of the reference matrix SSP of about 120 μg is weighed in the sample cups. A volume of approximately 25 μl of the solutions containing bisphenol A and bisphenol S is added to the sample cups the day before the analysis and dried over night in a desiccator. Each calibration level is prepared with a solution of different analyte concentration. Before quantification, new calibration samples are prepared.

If not otherwise mentioned, 10 μl of TMSH (10% in methanol/water) or 5 μl of TMAH (10% water) is added to

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