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1 **Rapid multi-analyte quantification of benzophenone, 4-methylbenzophenone and**
2 **related derivatives from paperboard food packaging**

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13
14 **Abstract**

15 Photo-initiators are used in printing inks hardened with UV light and one of the most
16 commonly used photo-initiators is benzophenone (BP). Recent notifications under the
17 Rapid Alert System for Food and Feed have shown migration of 4-methylbenzophenone
18 (4-MBP) from packaging into cereals. A specific migration limit exists for BP of 0.6 mg
19 kg⁻¹ for its use as an additive in plastics. There is no specific European legislation
20 covering cardboard boxes and/or printing inks for food contact use. However, due to the
21 high levels detected, the European Food Safety Authority (EFSA) published
22 recommendations and the Standing Committee for the Food Chain and Animal Health
23 endorsed a limit of 0.6 mg kg⁻¹ for the sum of BP and 4-MBP. While studies have been

1 published on photo-initiators in the past, there is a fundamental lack of data on 4-MBP
2 especially for its combined analysis with others. We present an HPLC method with diode
3 array detector to simultaneously determine the levels of BP, 4-MBP as well as 7 other
4 possible derivatives from secondary packaging for food applications. The method was
5 tested and applied to 46 samples of paperboard for secondary packaging collected both
6 from supermarkets and directly from a paperboard supplier. In addition, a survey was
7 conducted on recycled paperboard (n= 19) collected from a supplier, to evaluate the
8 background quantity of BP and other derivatives in recycled board. The most abundant
9 photo-initiator found in the survey was BP, in 61% of samples, and 4-MBP was found in
10 30% of the samples. It seems that these compounds are used to replace one another.
11 Other derivatives were found in minor quantities. Traces of BP were also found in 42%
12 of the samples of recycled, unprinted board.

13
14 **Keywords:** benzophenone; 4-methylbenzophenone; photo-initiators; recycled board

15 **Running head:** Multi-analyte quantification of photo-initiators

1 Introduction

2 German authorities recently reported a high migration of 4-methylbenzophenone (4-
3 MBP) from packaging into cereals using the Rapid Alert System for Food and Feed
4 (RASFF). Following this alert, the European Commission asked the European Safety
5 Authority to evaluate whether 4-MBP should be included in the current tolerable daily
6 intake (TDI) for benzophenone (BP) and hydroxybenzophenone. The risk of the presence
7 of 4-MBP was also to be evaluated (EFSA 2009a). Later, the Scientific Panel on food
8 contact materials, enzymes, flavourings and processing aids (CEF) published a scientific
9 opinion on its toxicity, concluding that short term consumption of cereals containing 4-
10 MBP at observed levels should not constitute a risk to the population. However, if the
11 consumption of the compound is continuous, more data on the occurrence as well as
12 proper toxicity data of the compound is needed (EFSA 2009b).

13 Photo-initiators are used in inks hardened with ultraviolet (UV) light (Anderson
14 and Castle 2003). Their benefits include reduced drying times compared to water-based
15 coatings, allowing a continuous production process (Anderson and Castle 2003). As UV
16 inks usually do not contain any traditional organic solvents, they are considered
17 environmentally friendly (Papilloud and Baudraz 2002). UV inks are used to produce an
18 appealing glossy cover to the printed packaging, especially for paperboard, and high
19 amounts of photo-initiators are used for this purpose in the ink preparation. One of the
20 most known photo-initiators is BP. It has been determined to migrate from printed board
21 into the food as it is neither totally used up during the printing process, nor removed
22 afterwards, nor irreversibly bound into the print film layer. The migration of photo-
23 initiators from the packaging to the food through the vapour phase is possible even from

1 the secondary packaging, i.e. when the ink is not in direct contact with the food (Johns et
2 al. 2000, Anderson and Castle 2003, Triantafyllou et al. 2007, Pastorelli et al. 2008,
3 Rodríguez-Bernaldo de Quirós et al. 2009). The rate of the migration of photo-initiators
4 through the vapour phase is highly influenced by their boiling point and the vapour
5 pressure as well as by the type of the food package. The commonly used BP is known to
6 migrate easily through the vapour phase and it has been substituted with other derivatives
7 over the last few years (Pastorelli et al. 2008).

8 4-MBP is an example of a photo-initiator used either instead or, more rarely,
9 together with BP (EFSA 2009a). At the present time, printing inks and/or cardboard
10 boxes are not covered by specific European legislation on food contact materials.
11 Nevertheless, the use of printing inks has to comply with the general rules of Regulation
12 (EC) No 1935/2004 and with good manufacturing practice as laid down in Commission
13 Regulation (EC) No 2023/2006 (EFSA 2009a). The specific migration limit (SML) for
14 BP is 0.6 mg kg^{-1} for its use as an additive in plastics. Recently, due to the high levels
15 detected, the European Food Safety Authority (EFSA) published recommendations and
16 the Standing Committee for the Food Chain and Animal Health endorsed a limitation to
17 0.6 mg kg^{-1} for the sum of BP and 4-MBP (SANCO 2009).

18 As the paperboard of secondary packaging is widely printed with the UV inks, it
19 is important to bear in mind that the most commonly used raw material for paperboard is
20 recycled and there the levels of photo-initiators, like BP, might persist or even
21 accumulate (Anderson and Castle 2003). Recycled board is commonly used in direct
22 contact with dry foodstuffs, like flour and pasta, but also with fast food items, i.e. short
23 duration contact food types, like pizzas. Usually a functional barrier, e.g. plastic or

1 aluminium foil, is used between fatty or aqueous foodstuff and the recycled material to
2 avoid direct contact (Binderup et al. 2002). BP is known to migrate easily through
3 polypropylene film but multilayer material has shown to inhibit the migration efficiently
4 (Pastorelli et al. 2008).

5 Studies have been conducted widely into the levels and behaviour of photo-
6 initiators in printing inks used for food packaging materials, including migration through
7 direct contact and the vapour phase, as well as stability. Some studies have focused on
8 method development to determine the different kinds of photo-initiators, e.g. after the
9 recent isopropyl thioxanthone (ITX) alert (Johns et al. 2000, Anderson and Castle 2003,
10 Sagratini et al. 2006, Triantafyllou et al. 2007, Pastorelli et al. 2008, Sanches-Silva et al.
11 2008a, Sanches-Silva et al. 2008b, Rodríguez-Bernaldo de Quirós et al. 2009, Wang
12 2009). Data on 4-MBP is remarkably scarce, therefore this paper presents a high
13 performance liquid chromatography (HPLC) analytical method with diode array detector
14 (DAD) to simultaneously determine the levels of benzophenone, 4-methylbenzophenone
15 (Fig. 1) as well as 7 other possible derivatives from secondary packaging for food
16 applications: 4-hydroxybenzophenone, methyl-2-benzoylbenzoate, 2-
17 hydroxybenzophenone, 4-benzoylbiphenyl (PBZ), 4,4'-bis(diethylamino)benzophenone,
18 2-ethylhexyl-4-(dimethylamino)benzoate and benzophenone acrylate (BPacr).
19 Identification of the compounds was verified with GC-MS. Altogether, 46 samples of
20 paperboard for secondary packaging were collected both from food bought at the
21 supermarket and directly from the paperboard supplier. The contents of BP, 4-MBP and
22 other derivatives were studied. In addition, a survey was conducted on recycled
23 paperboard (n = 19) collected from the supplier in order to evaluate the background

1 quantity of BP and derivatives before the printing process. In a trial experiment, the
2 choice of solvent was studied by replacing acetonitrile with methanol.

3 4 **Materials and methods**

5 *Packaging and food samples*

6 The samples for the study were collected from the supermarkets (with the food, n = 22)
7 and some packages were acquired from the industrial production lines prior to
8 introducing the foodstuff (n = 24) (Table 1). As paperboard for secondary packages is
9 commonly made from recycled material, a survey was also conducted with recycled,
10 unprinted board material (n = 19).

11 12 *Chemicals and standards*

13 Acetonitrile (ACN, CAS n 75-05-8) was supplied both from Carlo Erba and Advanced
14 Biotech and methanol (CAS n 67-56-1) was supplied from Sigma-Aldrich. Solvents used
15 were high purity grade. Ultrapure water was prepared with Milli-Q filter system
16 (Millipore, Bedford, MA, USA).

17 Standards 4-hydroxybenzophenone 98% (CAS n 1137-42-4), methyl-2-
18 benzoylbenzoate 97% (606-28-0), 2-hydroxybenzophenone 99% (117-99-7), 4-methyl
19 benzophenone (4-MBP) 99% (134-84-9), 4-benzoylbiphenyl (PBZ) 99% (2128-93-0),
20 4,4'-bis(diethylamino)benzophenone 99+% (90-93-7), and 2-ethylhexyl-4-
21 (dimethylamino)benzoate 98% (21245-02-3) were obtained from Aldrich and
22 benzophenone (BP) ≥99% (119-61-9) was supplied by Fluka. Benzophenone acrylate
23 (BPacr) was obtained directly from a supplier (CAS 59626-79-8).

1

2 ***Standard solutions***

3 A stock solutions (2000 $\mu\text{g mL}^{-1}$ of ACN) of 4-hydroxybenzophenone, methyl-2-
4 benzoylbenzoate, 2-hydroxybenzophenone, 4,4'-bis(diethylamino)benzophenone and 2-
5 ethylhexyl-4-(dimethylamino)benzoate we prepared and diluted into the intermediate
6 standard solutions (100 $\mu\text{g mL}^{-1}$ of ACN). Also the stock solutions of BP, 4-MBP and
7 PBZ (900 $\mu\text{g mL}^{-1}$ of ACN) as well as of BPacr (2.4 mg mL^{-1} of ACN) were prepared and
8 diluted into the intermediate standard solutions (180 $\mu\text{g mL}^{-1}$ of ACN; for BPacr 120 and
9 360 $\mu\text{g mL}^{-1}$ of ACN). The calibration curves were obtained with further dilutions (in
10 ACN) from the intermediate standard solution in the ranges of 4.5-117 $\mu\text{g mL}^{-1}$ (8-14
11 points) for BP, 4-MBP and PBZ and 12-250 $\mu\text{g mL}^{-1}$ (11 points) for BPacr. For methanol
12 studies, separate standard solutions were made into methanol. Solutions were stored
13 refrigerated in the dark.

14
15 ***Sample preparation***

16 The board material from the food packages, and in some cases the food as well, were
17 analyzed with modifications of methods previously used for BP and other photo-initiators
18 (Pastorelli et al. 2008, Sanches-Silva et al. 2008a). Two different samples of 0.5 dm^2
19 were prepared from each packaging material. Each sample was cut into small pieces,
20 placed into a glass container and extracted tightly-closed with acetonitrile ($V = 20 \text{ mL}$)
21 for 24 h at 70°C. The extract was cooled down to room temperature, filtered through 0.45
22 μm PTFE filter and analyzed with HPLC-DAD.

1 For some samples (see Table 1), the content of photo-initiators in the food was
2 also analyzed. The food was homogenized and a portion ($m = 1$ or 4 g) was placed into a
3 glass container and extracted tightly-closed with acetonitrile ($V = 3$ mL) for 24 h at 70°C .
4 The extract was cooled down to room temperature, filtered through $0.45\ \mu\text{m}$ PTFE filter
5 and analyzed with HPLC-DAD.

6 Primarily, the paperboard extractions were done with acetonitrile ($V = 20$ ml) as
7 described above, but the use of methanol ($V = 20$ ml) as extraction solvent was also
8 tested.

9 10 *Chromatographic conditions*

11 *HPLC-UV*

12 Analytical chromatographic analyses were performed with different HPLC systems using
13 a method adopted and modified from a previously published method for benzophenone
14 only (Pastorelli et al. 2008).

15 The used HPLC was an Agilent technologies 1200 series degasser and diode array
16 detector equipped with Hewlett Packard 1100 series binary pump and autosampler. The
17 software was Chemstation (2001-2007, Rev.B.03.01[137]). The column was an Eclipse
18 XDB-C18 (250×4.6 mm i.d.; $5\ \mu\text{m}$; Agilent Technologies). The tests were performed
19 separately for each system with different standards and calibration curves.

20 The binary mobile phase consisted primarily of acetonitrile and water. The
21 gradient elution was from 50% acetonitrile in water (v/v) to 100% acetonitrile in 10 min
22 (linear); 100% acetonitrile was kept for 5 min (isocratic), back to 50% acetonitrile in 1
23 min (linear) and it was kept for 4 min (isocratic) before the next run. The total run time

1 was 20 minutes. The detection wavelengths varied according to the HPLC system used
2 and the calibration curves were done separately for each compound and instrument using
3 the appropriate wavelength (see Table 2 for precise numbers). The flow rate was 1.0 mL
4 min^{-1} and the injection volume 50 μL .

5 Additional experiments were done by replacing acetonitrile with methanol,
6 otherwise keeping the same method parameters. The samples for this experiment were
7 chosen among the total 46 samples included to the survey (samples in which BP or 4-
8 MBP was present) and further identified with letters A-J (as only the difference between
9 two solvents was under interest). With these samples (A-J), we also studied the stability
10 of the samples.

11 *GC-MS*

12 The gas chromatograph system consisted of a Hewlett Packard 6890 Series gas
13 chromatograph equipped with an autosampler and a programmed split/splitless injector,
14 and a Hewlett Packard 5973 mass selective detector with MSD ChemStation D.02.00.275
15 software. The column was DB-5HT (5%-Phenyl-methylpolysiloxane, Agilent J&W, 30 m
16 \times 0.25 mm i.d., 0.1 μm thickness).

17 The carrier gas was helium with flow of 1.3 ml min^{-1} . The injector temperature
18 was 250°C and the samples were injected with a split mode (ratio 1:40). The injection
19 volume was 1 μL . The oven was running with temperature programme: 100°C for 2 min,
20 followed by a rate of 10°C min^{-1} up to 250°C, which was held for 10 min. Total run time
21 was 27 min. The mass spectra were obtained with a mass selective detector under
22

1 electron impact ionization at a voltage of 70 eV and data acquisition was at a scan rate of
2 0.45 s⁻¹.

3 4 **Results and discussion**

5 With the method described here, it was possible to simultaneously analyse the
6 contents of benzophenone and 4-methylbenzophenone as well as seven related
7 derivatives.

8 9 *Optimization of the extraction and chromatographic methods and the method* 10 *validation*

11 The single-solvent extraction of samples was carried out for 24 h at 70 °C which
12 has previously proved to provide complete extraction of BP (Pastorelli et al. 2008).
13 Different elution programmes were tested for the selected column and compounds.
14 Finally, the HPLC method introduced here managed to separate BP, 4-MBP and 7 other
15 related derivatives within a rather short time of analysis (Figures 2 and 3). The retention
16 time for BPacr overlapped with the PBZ and 4,4'-bis(diethylamino)benzophenone, but
17 the identification was possible because their UV spectra differed (Fig. 4). Further, BPacr
18 was not found to be present in the same samples as PBZ and 4, 4'-
19 bis(diethylamino)benzophenone. With the current method, BPacr characteristically
20 creates a bunch of peaks in HPLC, which facilitates its identification.

21 The stability of the sample extracts was studied according to their contents of BP
22 and 4-MBP (Fig. 5). The extracts were analysed both immediately and after three to five
23 months of storage (in hermetically closed vials in 4°C or in room temperature). The

1 analysed contents of BP and 4-MBP varied only up to 4.6 % (variation of BP in sample
2 E) between two measurements (analyses done in duplicates in both times) when the
3 contents were 0.20 mg dm⁻² or higher. Further, it could be seen that as the concentrations
4 of analytes decreased, the variation between immediate and after storage analyses
5 increased.

6 Calibration curves were constructed for BP, 4-MBP, PBZ and BPacr with
7 different HPLC systems (see Table 2). Detection (LOD) and quantification limits (LOQ)
8 were established according to the Guidelines of the American Chemical Society (ACS)
9 (MacDougall et al. 1980). BPacr is a mixture of oligomers of which it was possible to
10 create the calibration curve integrated over the cluster of peaks (Table 2, Fig. 3).

11 *The effect of solvent in extraction and elution*

12 Due to the recent shortage in the production and on the market of acetonitrile (Tullo
13 2008), we tested the possibility of replacing it with methanol during the extraction and
14 elution (samples were done in duplicates). The results were relatively similar for BP and
15 4-MBP. The retention times turned out to be a bit longer for all the standards with
16 methanol, but the measured concentrations (calculated from the peak areas) remained
17 quite stable. BP results achieved with the different extraction and elution solvents
18 differed on average 6% in respect to the peak areas (C, F, G), but more with some
19 samples (A: 22% and E: 62%). The measurements made for the five samples containing
20 4-MBP differed from 2.3 to 9.4% in respect to the peak areas. The most evident
21 difference between the solvents was the elution of BPacr. The cluster of peaks observed
22 with acetonitrile (Fig. 3) is lost when eluted with methanol; BPacr gave only one peak
23

1 with methanol. It is accordingly recommended to use the same solvent both for extraction
2 and in elution, and as a solvent when preparing the standards, especially in the analysis of
3 BP.

4 5 *Analysis of samples*

6 *The contents of benzophenone and derivatives*

7 The most abundant UV-initiator found in this survey was BP. We found it in quantitative
8 levels in 27 samples (59%) of the total 46 samples, whereas 4-MBP was found in 14
9 samples (30%) (Table 1). It appeared that BP and 4-MBP were not usually present in the
10 same samples. When the level of BP is high in the sample, there is no (or only traces of)
11 4-MBP, and vice versa. It seems that these compounds are used to replace one another.

12 Measurable levels of PBZ were found in three samples, #11; 13 and 21, where the
13 levels of the compound were 97, 21 and 36 mg m⁻², respectively. Identification was
14 verified with GC-MS. In four samples, #14-17, we found BPacr in contents of 151.5;
15 792.6; 819.5 and 815.1 mg m⁻², respectively. The other benzophenone related derivatives
16 included in the analysis were not found in the products in the survey.

17 Some of the carton packages were printed with two different techniques. Part of
18 the package was printed with UV-ink to achieve a shiny result whereas another part was
19 printed with conventional water-based ink not containing photo-initiators. Theoretically,
20 this should have given rise to differences in the contents of photo-initiators in different
21 parts of packages. Contrary to assumptions, in spite of different printing ink types on
22 different parts of the package no differences could be seen between different parts of

1 packages. This gives further proof of the migration of BP (Rodríguez-Bernaldo de Quirós
2 et al. 2009).

3 In the survey of recycled, unprinted board material (n = 19), BP was found in
4 detectable levels in nearly half of the samples (42 %, 8 samples). The content of BP in
5 those samples varied from 0.57 to 3.99 mg m⁻² (the board material varied from 2.78 to 18
6 mg kg⁻¹ in weight). Other derivatives studied here were not found in measurable levels
7 from recycled, unprinted board material.

8 After finding high contents of BP in sample 1 and 4-MBP in sample 2, we also
9 analysed the products. Despite high contents of photo-initiators in the package and their
10 high migration ability, we found only very scarce levels of photo-initiators in the
11 homogenized product (below the SML (SANCO 2009)). Therefore, the plastic film used
12 as primary packaging in direct contact with the product was also analysed. The analyses
13 were done with the attenuated total reflection (ATR-IR) spectroscopy which is used for
14 surface analysis. The plastic film in sample 2 was found out to be polypropylene whereas
15 the plastic film in sample 1 was found to be consisted of different layers one side being
16 polyethylene terephthalate (PET) and the other side polypropylene (PP). Hence, it
17 seemed to be a multilayer material preventing the migration of BP. Multilayer material
18 consisting of PET/silic oxide/PP has been reported to prevent BP migration (Pastorelli et
19 al. 2008).

20 21 *Additional drying step for inks including photo-initiators*

22 The board samples acquired from the industrial production lines included samples from a
23 test of the different oven treatments for drying the UV ink after the printing process

1 (Table 3). The additional drying procedures were unable to push the printing process to
2 decreased levels of BP and 4-MBP. The most drastic treatment (Table 3, treatment IV)
3 with the most severe oven drying failed to produce lower levels of these photoinitiators.
4 The content of BP was initially very low and its concentration was barely affected by the
5 treatments. The concentrations of 4-MBP were initially higher but none of the additional
6 treatments decreased the levels of 4-MBP even by half, the lowest achieved concentration
7 was still as high as 65% of the initial concentration. BPacr turned out to be most
8 abundant after treatment III (Table 3), the same treatment where 4-MBP levels were the
9 lowest which suggests that BPacr might be a product of other photoinitiators. Following
10 these results, it can be claimed that additional oven drying after printing does not bring
11 any further benefits.

12 **Conclusions**

13 The described method allowed a rapid multi-analyte quantification of benzophenone, 4-
14 methylbenzophenone and 7 other possible derivatives from paperboard secondary
15 packaging for food applications by HPLC-DAD. The survey was carried out with 46
16 samples of paperboard for secondary packaging. Results showed that BP and 4-MBP are
17 not usually present in the same packaging, but rather seem to replace one another. More
18 than half the samples included BP, 30% of samples included 4-MBP, 9% of the samples
19 included BPacr and 7% of the samples included PBZ. This survey indicates that,
20 generally a high concentration of one photo-initiator and traces of other possible
21 substitutes are found. Those traces might also exist as residual levels of formerly used
22 printing inks remaining on recycled paperboards, as demonstrated by the survey on non-
23

1 printed recycled paperboard. For this reason, we might even find traces of photo-initiators
2 coming from recycled paperboard when no UV-inks were used. The ability of the photo-
3 initiator (used in the printing process) to migrate through the vapour phase should be
4 considered in a risk evaluation together with the right choice of a primary packaging to
5 assure the right protection to the packaged food. The responsibility to find the right
6 photo-initiators to use and/or avoid belongs to the whole production line including the
7 food industry and the suppliers.

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3 **1 Figure legends**
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8 3 Figure 1. Chemical structures of the photo-initiators BP (1) and 4-MBP (2).
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12 5 Figure 2. HPLC chromatogram of eight different benzophenone related standards (c ~
13 100 µg/mL).
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20 8 Figure 3. HPLC spectrum of BPacr (c = 100 µg/mL)
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24 10 Figure 4. UV spectra of BPacr, PBZ and 4,4'-bis(diethylamino)benzophenone.
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29 12 Figure 5. The content of (a) BP and (b) 4-MBP in samples A-J. Grey bars represent
30 analyses done immediately after extracting samples, white bars represents analyses on
31 hermetically closed extracts stored 3-5 months in dark and cold (A-G) or at room
32 temperature (H-J).
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Table 1. Contents of BP and 4-MBP in 46 paperboard samples.

Sample number	Sample type	Supplier	BP ^b (mg dm ⁻²)	4-MBP (mg dm ⁻²)
1 ^a	cake	Supermarket	2.56	n.d.
2 ^a	cake	Supermarket	0.07	1.47
3	cereals	Supermarket	n.d.	n.d.
4	cereals	Supermarket	n.d.	n.d.
5	cookies	Supermarket	n.d.	n.d.
6	dried fruits	Supermarket	n.d.	n.d.
7	dried fruits	Supermarket	n.d.	n.d.
8	cookies	Supermarket	n.d.	n.d.
9	cake	Supermarket	2.10	n.d.
10	cake	Supermarket	0.06	2.24
11	cereals	Supermarket	0.05	n.d.
12	crêpes	Supermarket	3.38	n.d.
13	cake	Industry	0.04	1.69
14	cake	Industry	0.10	4.41
15	cake	Industry	0.22	n.d.
16	cake	Industry	n.d.	n.d.
17	cake	Industry	0.06	n.d.
18	coffee	Industry	3.99	0.05
19	cake	Industry	0.10	4.33
20	cookies	Industry	1.57	n.d.
21	cookies	Industry	0.02	n.d.
22	cake	Industry	0.09	0.98
23	cake	Industry	0.21	1.10
24	cake	Industry	2.23	n.d.
25	cake	Industry	n.d.	n.d.
26	cake	Industry	3.21	n.d.
27	cake	Industry	1.43	n.d.
28	cake	Industry	3.02	n.d.
29	cake	Industry	2.97	n.d.
30	cake	Supermarket	1.66	n.d.
31	cake	Supermarket	3.84	0.05
32	cake	Supermarket	n.d.	n.d.
33	chocolate	Supermarket	1.07	n.d.
34	cake	Industry	0.02	1.00
35	cake	Supermarket	0.35	1.04
36	cake	Industry	2.98	n.d.
37	cake	Supermarket	n.d.	n.d.
38	chocolate	Industry	n.d.	n.d.
39	chocolate	Industry	n.d.	1.48
40	chocolate	Industry	n.d.	n.d.
41	chocolate	Industry	n.d.	0.03
42	chocolate	Industry	n.d.	1.47
43	nuts	Supermarket	n.d.	n.d.
44	pastry	Supermarket	n.d.	n.d.
45	pastry	Supermarket	n.d.	n.d.
46	cake	Supermarket	n.d.	n.d.

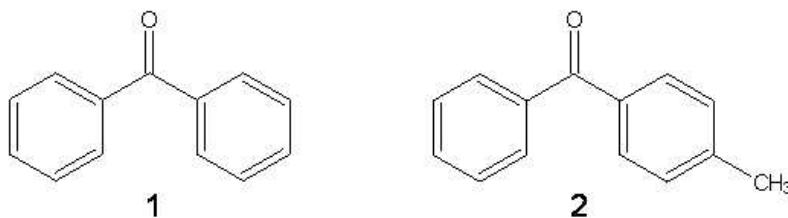
^a The food was analysed^b n.d. = not detectable

Table 2. Validation parameters for the method to measure benzophenone and other derivatives in food packaging paperboard.

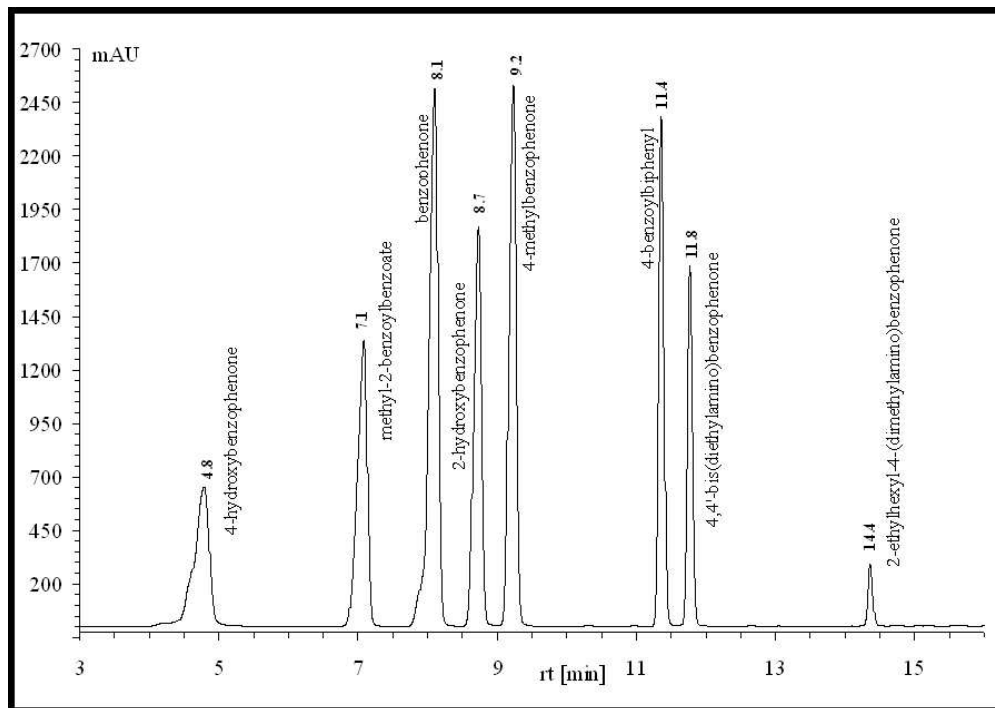
	Intercept	Slope	r^2	Range [mg L ⁻¹]	LOD [mg L ⁻¹]	LOQ [mg L ⁻¹]
BENZOPHENONE						
wl = 256 nm, rt = 8.03 min	154.42	265.88	0.9996	0.46-118.4	0.046	0.14
4-METHYL BENZOPHENONE						
wl = 260 nm, rt = 9.1 min	290.41	237.56	0.9991	0.46-118.3	0.046	0.14
BENZOPHENONE ACRYLATE						
wl = 256 nm, rt = 10.8-12 min	151.3	74.36	0.9996	0.45-253.05	1.22	3.67
4-BENZOYLBIPHENYL						
wl = 290 nm, rt = 11.15 min	844.42	201.01	0.9916	0.45-118.0	0.045	0.14

Table 3. Levels of three photo-initiators on printed paperboard samples after different additional drying trials.

	BP	4-MBP	BPacr
	(mg dm⁻²)		
Basic procedure	0.10	4.41	1.52
Additional treatments (oven drying)			
I: 200 °C for 10 min	0.12	4.38	1.20
II: 200 °C for 2 x 10 min	0.13	4.64	1.26
III: 200 °C for 20 min	0.14	2.86	3.25
IV: 200 °C for 2 x 20 min	0.12	4.49	1.19

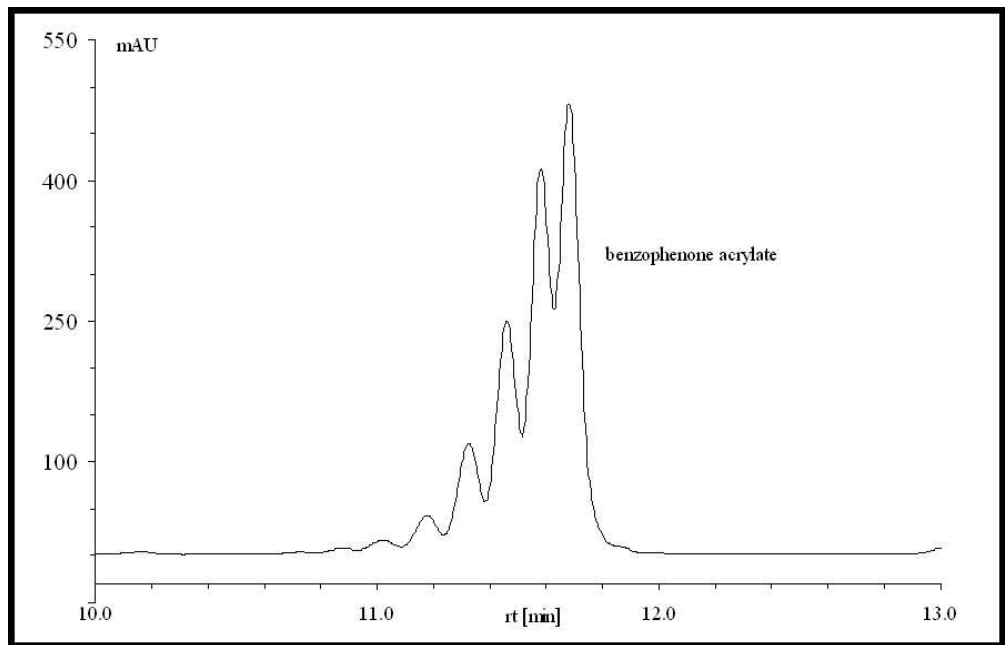


Chemical structures of the photo-initiators BP (1) and 4-MBP (2).
173x79mm (96 x 96 DPI)



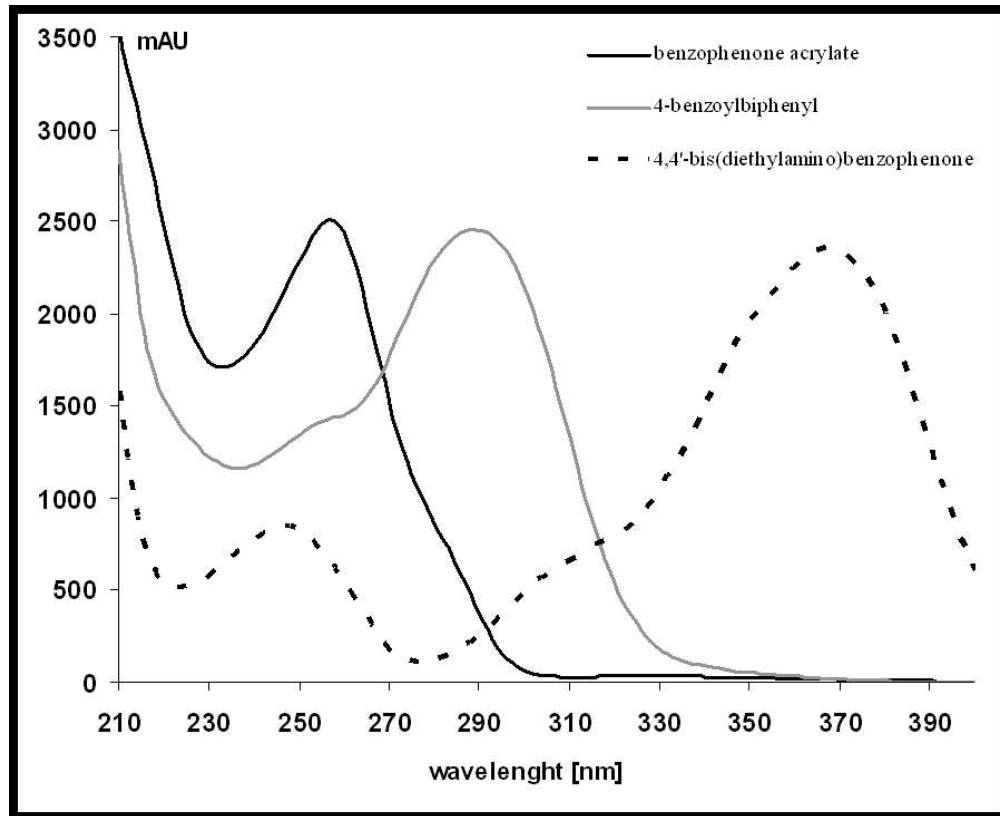
HPLC spectrum of eight different benzophenone related standards.
152x107mm (150 x 150 DPI)

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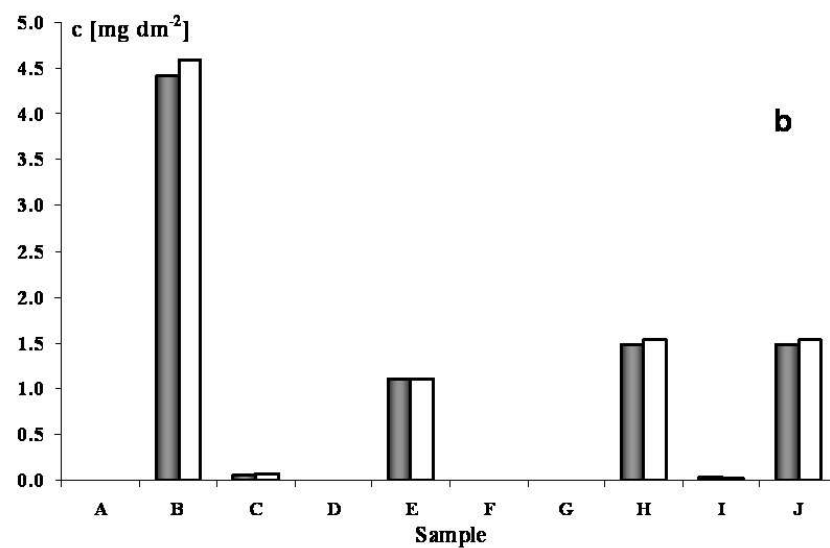
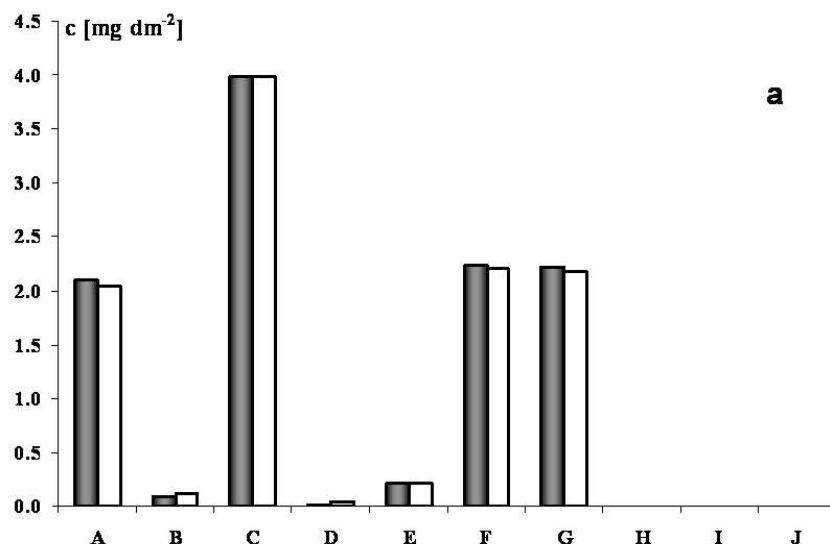


HPLC spectrum of BPacr
152x97mm (150 x 150 DPI)

Review Only



UV spectra of BPacr, PBZ and 4,4'-bis(diethylamino)benzophenone.
152x123mm (150 x 150 DPI)



The content of (a) BP and (b) 4-MBP in samples A-J. Grey bars represent analyses done immediately after extracting samples, white bars represents analyses on hermetically closed extracts stored 3-5 months in dark and cold (A-G) or at room temperature (H-J).
150x194mm (150 x 150 DPI)