Analysis of Printing Ink Components from Food Packaging Materials by GC/MS/MS

Application Note

Food Safety

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Abstract

A method has been developed on the Agilent 7000 GC Triple Quadrupole GC/MS/MS system for the analysis of foods for 20 chemicals that may be present in printing inks applied to the external surface of cartonboard packaging material. These substances may diffuse through the cartonboard or set-off onto the food contact surface and then migrate into food. The method described is suitable for the reliable determination of ink substances in packed foods at single-figure parts-per-billion (ppb, µg/kg) levels.

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Introduction

Printing inks used on the external surface of food packaging can contain many different substances including photoinitiators, plasticisers, binders, colorants, pigments, solvents, and driers [1], and these may transfer into the foodstuff through three different methods of migration:

- Direct contact between the printing ink and the foodstuff (unlikely to occur)
- Migration through the packaging (including transfer through some secondary packaging too)
- Migration through set-off (unintentional transfer of ink by direct contact between the printed surface and the food contact surface, before the food is packed)

Previous reported methods of analysis have included detection of single substances such as benzophenone by GC/MS [2] or a number of related substances such as benzophenone, 4-methylbenzophenone, and related derivatives also by GC/MS [3]. Analysis of foods for ink substances is particularly demanding because of three factors:

1. Many substances have a low level of interest - typically 10 ppb (10 µg/kg food) or lower is required
2. The interest in a wide range of ink substances limits the opportunities for selective sample extraction and sample clean-up methods, resulting in rather crude sample extracts
3. A wide range of food types are packaged in printed packaging including composite foods, for example, ready-meals, and this, coupled with (2), results in many co-extractives as possible interferences

The impact of these factors is that GC/MS can struggle to deliver the sensitivity and selectivity needed for a reliable identification and quantitation of ink substances in food survey samples. There is a need to confirm the identity of analytes based on their retention time and on the ratio of the main and secondary ions (quantifying and qualifying ions). The large quantity and nature of co-extractives and the low level of interest can make meeting identification criteria for both the retention time and the ion ratio problematic. For these reasons, we have investigated a GC/MS/MS method for testing foods for 20 printing ink components, because this technique should offer greater selectivity in separating the substances of interest from isobaric interferences. The Swiss Ordinance on printing inks [1] shows that hundreds of substances may be used in inks applied to the nonfood contact surface of packaging materials. Without prior knowledge of the ink composition, selecting those to test for can be likened to pulling a needle out of a haystack. Rather than randomly selecting substances to test, the 20 printing ink chemicals were chosen based on reports of their migration and based on the results of a separate research project screening a number of highly printed paper/board packaging materials (n = 50) to determine the potential migrants present.

Experimental

Sample Preparation

Food samples were purchased from a supermarket in the UK. These were removed from the packaging and homogenized using a food mixer. Figure 1 shows a flow diagram summarizing the sample preparation steps. A portion of the food sample was also over-spiked with the printing ink substances to allow recovery corrected concentrations to be calculated.

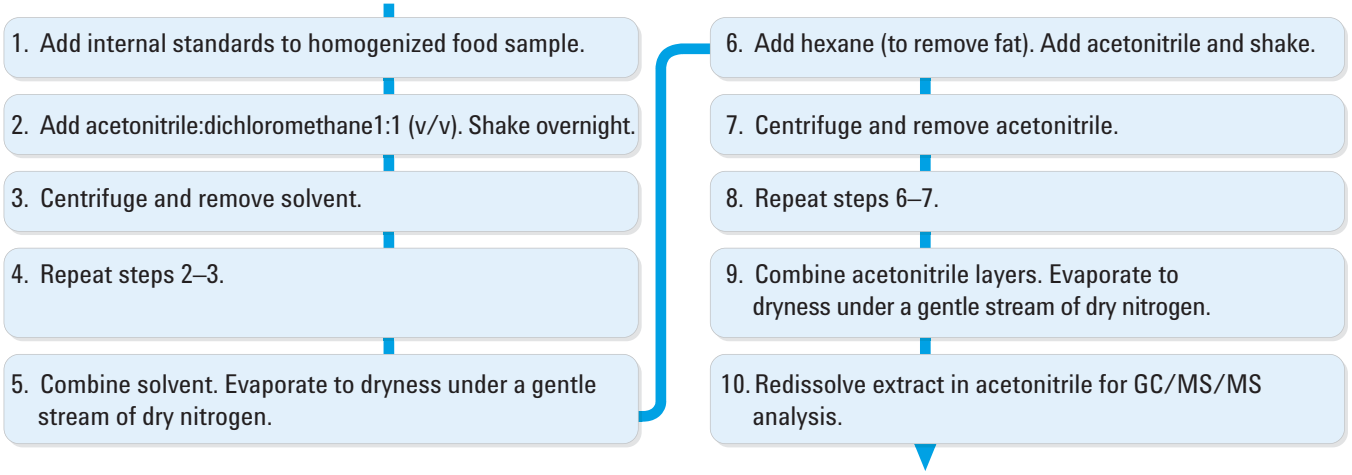


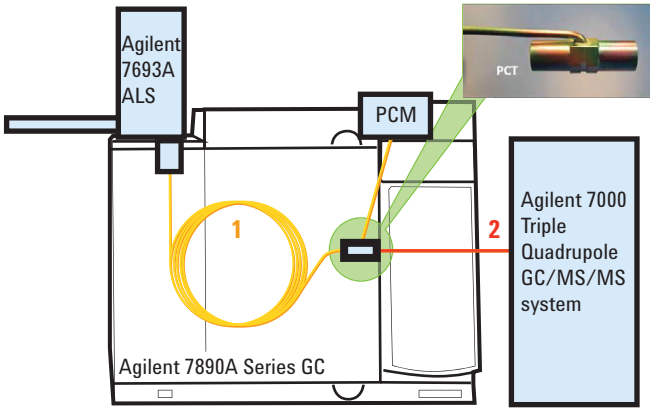
Figure 1. Flow diagram of the sample extraction and clean-up procedures.

Sample Analysis

The GC method employed post run, post column backflush. The use of backflush ensures that any high-boiling matrix material remaining on the column at the end of each run is quickly and efficiently removed (through the split vent) prior to the next injection in a sequence. Back flushing can provide:

- More consistent analyte retention times
- Robust chromatography and consistent analyte chromatographic peak shapes
- Prevention of high boiling matrix from contaminating the MS ion source
- Extended column life-time and reduced cycle times by removing the need for high-temperature bake-out between runs

Full GC analysis conditions are given in Table 1. The 7000 GC Triple Quadrupole GC/MS/MS system was operated in MS/MS electron impact (EI) ionization mode and analytes were detected and confirmed using Multiple Reaction Monitoring (MRM) mode with three transitions for each analyte. Full MS/MS conditions are given in Tables 2 and 3. Figure 2 shows a schematic diagram of the GC/MS/MS system hardware configuration.



1. Constant pressure, column 30 m × 0.25 mm id × 0.25 µm HP-5MS
2. Constant pressure, restrictor 1.0 m × 0.15 mm id deactivated fused silica

Figure 2. Schematic diagram of the GC/MS/MS hardware configuration.

Table 1. GC Conditions for the Analysis of Printing Ink Components

Column (1)	HP-5MS 30 m × 250 µm × 0.25 µm
Column (2)	Retention gap, 1 m × 150 µm un-coated deactivated fused silica
Capillary flow device	Pressure controlled tee (PCT) with Pneumatics Control Module (PCM)
Auto-sampler	Agilent 7693A
Injection volume	1 µL, hot splitless
Injection port	EPC Split/splitless
Injection port liner	Splitless, Deactivated 4 mm id single taper + glass wool
Inlet temperature	280 °C
Purge flow to split vent	50 mL/minute at 0.75 minutes
Carrier gas	Helium
Inlet pressure	17.0 psi
PCM pressure	4.5 psi
Oven program	100 °C for 1 minute then 10 °C/minute to 300 °C and held for 5 minutes
Post run time	3 minutes
Post run temperature	320 °C
Post run inlet pressure	1.0 psig
Post run PCM pressure	60.0 psig
MS transfer line temp	280 °C

Table 2. MS Conditions for the Analysis of Printing Ink Components

Electron energy	-70 EV
Tune	EI Autotune
EM gain	10–60
MS1 resolution	1.2 µ
MS2 resolution	1.2 µ
MRM transitions	Given in Table 3
Collision energies	Given in Table 3
Dwell times	25–100 ms
Collision cell gas flows	Nitrogen at 1.5 mL/minute, Helium at 2.25 mL/minute
MS temperatures	Ion source 280 °C, MS1 150 °C, MS2 150 °C

Results and Discussion

Method development

The GC/MS/MS method was developed by first using a multi-analyte solvent standard. Initially, retention time windows and parent ions were identified in full scan MS mode. Product ion spectra were generated by acquiring data at increments of 5 V in the range 5–50 V, and the product ions identified. Once estimated collision energies were determined, optimization was carried out using smaller incremental changes to collision energies. The MRM method was then built-up with the most intense MRM channel used for quantification and two others used for confirmation. Automated MRM optimization software was used to optimize dwell times. Figure 3 shows the extracted ion chromatograms of the quantitation ions for the solvent standard.

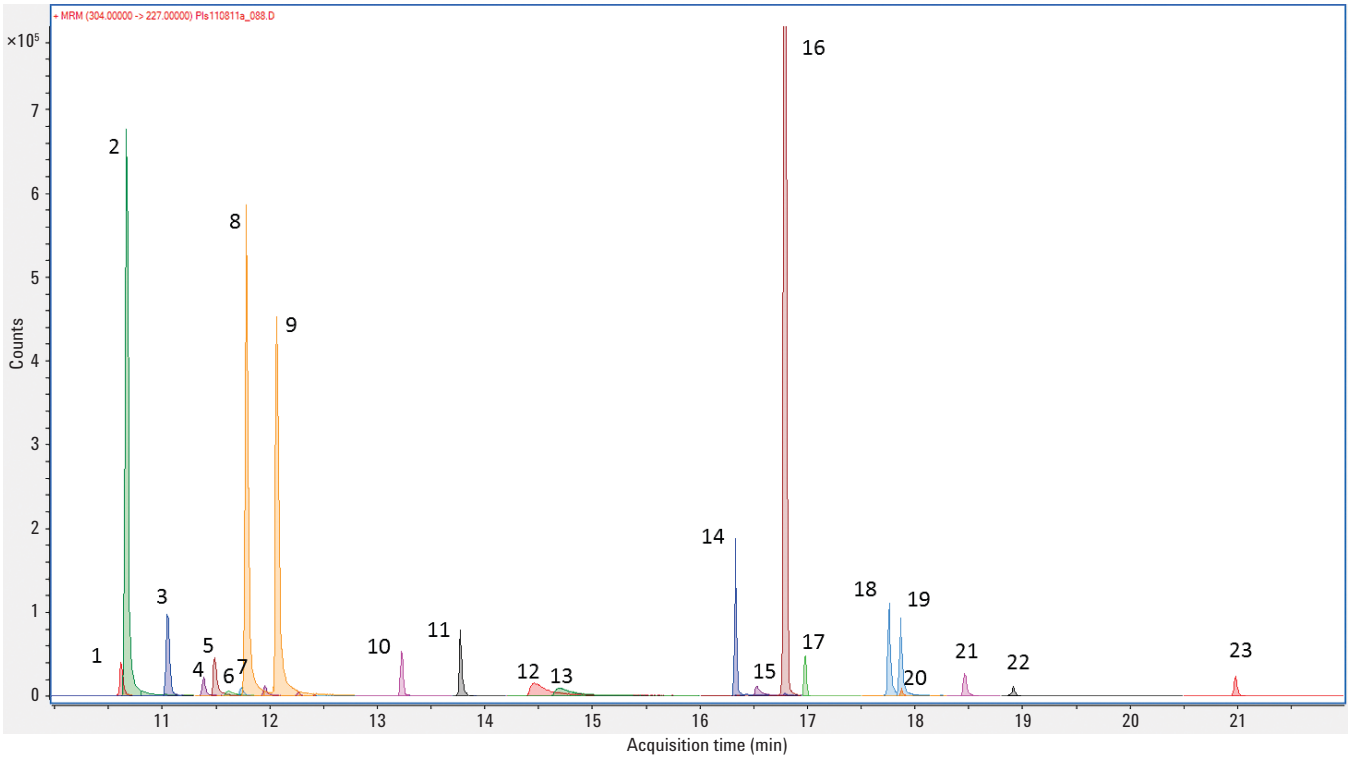


Figure 3. Extracted ion chromatograms of the quantitation ions for a multi-analyte solvent standard showing the 20 printing ink chemicals and three internal standards. (Peak numbers refer to Table 3).

Table 3. Analyte retention times, MS/MS transitions and collision energies

TS	Segment start time (minutes)	No.	Analyte	RT (minutes)	Quant precursor	Product	CE (V)	Qual precursor	Product	CE (V)
1	10.00	1	d_{10}-Benzophenone (IS)	10.75	192	110	10	192/192	82/54	34/50
		2	Benzophenone	10.81	182	105	12	182/182	152/77	36/36
		3	2-Methylbenzophenone	11.19	195	177	16	195/195	165/152	36/36
2	11.30	4	1-Hydrocyclohexyl phenyl ketone	11.52	99	81	7	99/99	79/55	16/16
		5	Ethyl-4-dimethylaminobenzoate	11.61	193	164	22	193/193	148/77	14/46
		6	N-Ethyl-p-toluene sulphonamide	11.68	184	91	16	184/184	155/65	1/40
		7	2-Hydroxybenzophenone	11.86	198	77	42	198/198	141/115	36/44
		8	3-Methylbenzophenone	11.92	196	181	3	196/196	153/119	24/10
		9	4-Methylbenzophenone	12.20	196	181	3	196/196	153/119	24/10
3	12.80	10	2,2-Dimethoxy-2-phenylacetophenone	13.37	151	105	12	151/151	91/77	14/26
4	13.70	11	Methyl-2-benzoylbenzoate	13.91	240	163	1	240/240	105/77	16/40
5	14.20	12	4-Fluoro-4-hydroxybenzophenone (IS)	14.44	216	121	12	216/216	93/65	34/44
		13	4-Hydroxybenzophenone	14.67	198	121	10	198/198	93/77	30/38
6	16.00	14	Bis-(2-ethylhexyl) fumerate	16.47	112	55	14	112/112	83/70	1/2
		15	Flavone (IS)	16.60	222	194	12	222/222	165/92	40/36
		16	2-Ethylhexyl-4-(dimethylamino)benzoate	16.92	277	165	10	277/277	164/148	30/30
7	16.95	17	2-Methyl-4-(methylthio)-2-morpholinoprophenone	17.10	128	84	14	128/128	69/56	26/24
8	17.50	18	4-Isopropylthioxanthone	17.88	254	239	14	254/254	196/105	36/30
		19	2-Isopropylthioxanthone	17.98	254	239	14	254/254	196/105	36/30
		20	Triphenyl phosphate	18.0	326	233	10	326/326	215/170	8/18
9	18.30	21	4-Phenylbenzophenone	18.57	258	181	12	258/258	153/105	32/36
10	18.80	22	2,4-Diethyl-9H-thioxanthen-9-one	19.0	268	253	20	268/268	237/165	40/46
11	20.50	23	4,4-(Methylphenylthio)benzophenone	21.09	304	227	16	304/304	184/105	38/18

Analysis of samples

A variety of food samples were tested using the method described. Two samples, frozen fish and pasta sheets, both in direct contact with the cartonboard primary packaging, were found to contain printing ink components. Concentrations and recoveries are given in Table 4. Benzophenone and 4-phenylbenzophenone were detected in the frozen fish and 4-phenylbenzophenone in the pasta sheets. The chemical structures are shown in Figure 4. Figure 5 shows the MRM transitions for the benzophenone and 4-phenylbenzophenone for the procedural blank, sample, over-spiked sample and solvent standard, showing the quantification channel and the two confirmation channels in compound at a glance mode. This is a very useful and fast way to scrutinize the data. Figure 6 shows the calibration curves for the two chemicals and shows good linearity (>0.999 in both cases) over the concentration ranges used (equivalent to 2.0–20 µg/kg for 4-phenylbenzophenone and 360–3600 µg/kg for benzophenone).

Table 4. Concentration and recoveries of the printing ink components detected in the samples

Sample type	Packaging	Printing ink component detected	Recovery corrected concentration (µg/kg)	Recovery (%)
Frozen fish	Cartonboard	Benzophenone	560	97
Frozen fish	Cartonboard	4-Phenylbenzophenone	11	96
Pasta	Cartonboard	4-Phenylbenzophenone	2.4	91

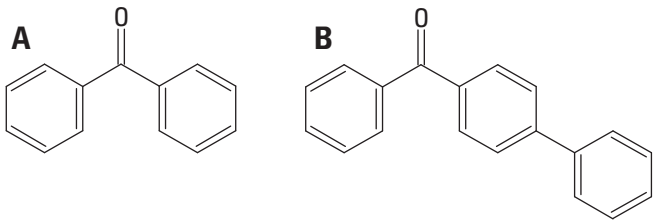


Figure 4. Chemical structure of a) benzophenone, b) 4-phenylbenzophenone.

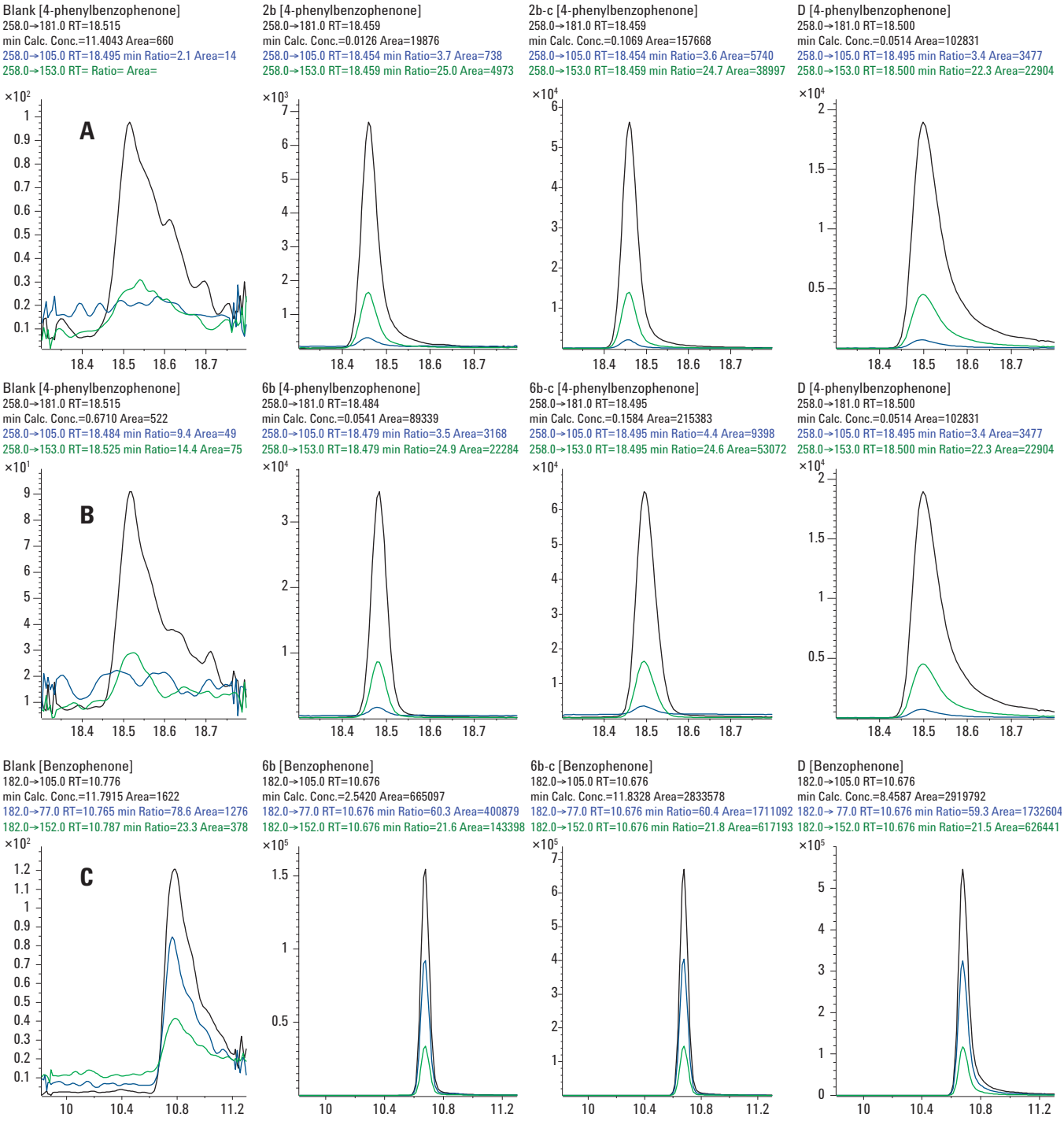


Figure 5. MRM transitions for the procedural blank, sample, over-spiked sample (10 µg/kg for 4-phenylbenzophenone and 1800 µg/kg for benzophenone) and solvent standard (equivalent of 15 µg/kg for 4-phenylbenzophenone and 2700 µg/kg for benzophenone), showing the quantification channel and the two confirmation channels for a) 4-phenylbenzophenone in the pasta sheet sample, b) 4-phenylbenzophenone in the frozen fish sample, c) benzophenone in the frozen fish sample.

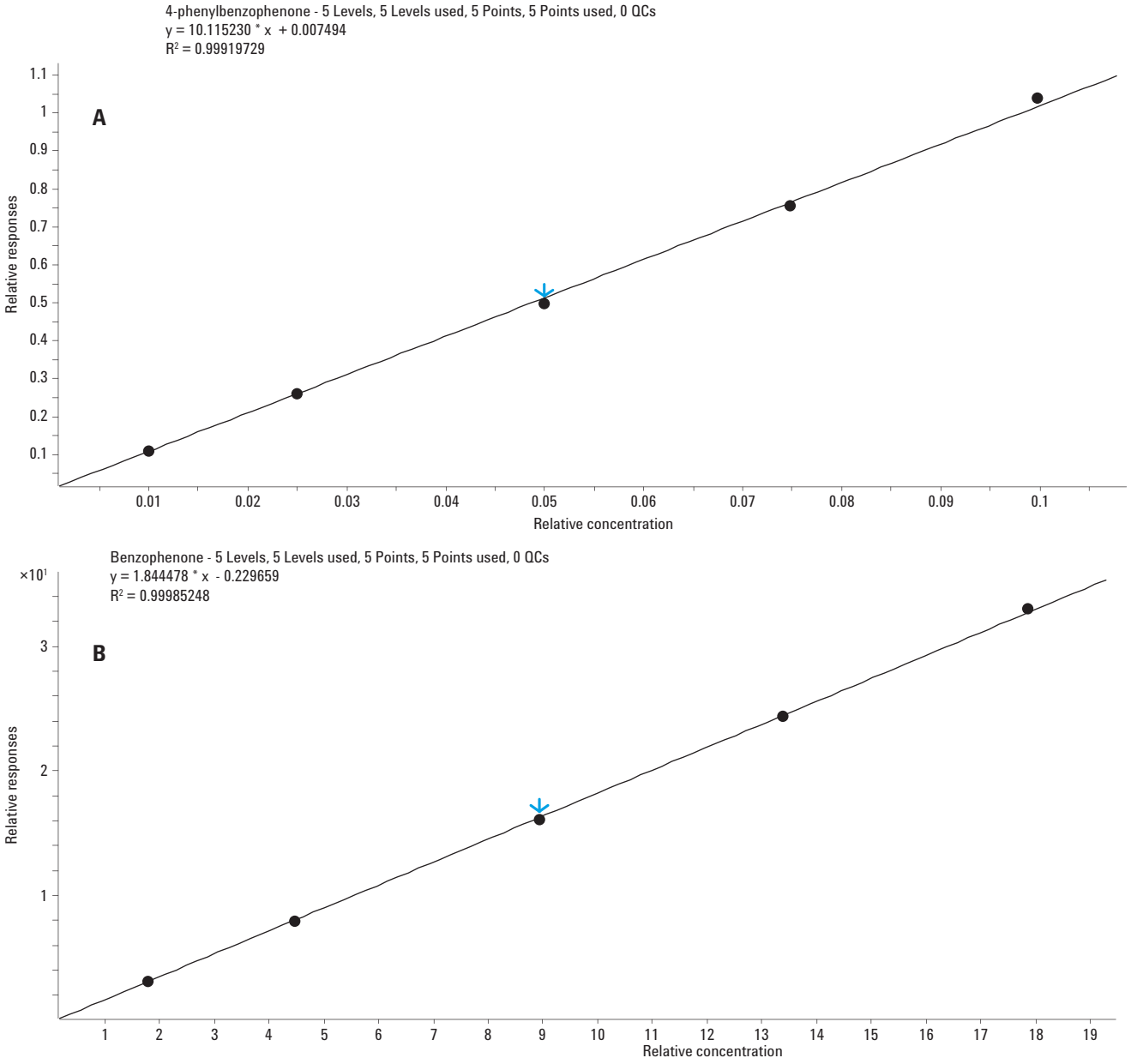


Figure 6. Calibration curves for a) 4-phenylbenzophenone (concentrations equivalent to 2.0–20 µg/kg), b) benzophenone (concentrations equivalent to 360–3600 µg/kg).

To put these results in to context, of the 10 RASFF alerts published on migration of printing ink compounds between October 2010 and March 2012, benzophenone was reported in four instances ranging in concentration from 430 µg/kg (ppb) in milk powder to 50 mg/kg (parts-per-million) in cinnamon.

The benzophenone concentration detected in the frozen fish sample in this application note was 560 µg/kg, which is close to the lower end of this range. 4-Phenylbenzophenone was reported in organic rice wafers with cocoa-hazelnut filling at 390 µg/kg and chocolate at 21 µg/kg. In this application note, 4-phenylbenzophenone was detected at 11 µg/kg or less.

Conclusions

Printing on packaging is very important to the manufacturer and the consumer, but components from the printing inks can migrate into the foodstuff. A method has been developed using GC/MS/MS analysis for 20 known printing ink components and has been demonstrated on real food samples.

References

1 Ordinance of the FDHA on Materials and Articles (817.023.21) found at: http://www.bag.admin.ch/themen/lebensmittel/04867/10015/index.html?lang=en

2 W.A.C. Anderson, L. Castle. Benzophenone in cartonboard packaging materials and the factors that influence its migration into food (2003) Food Additives and Contaminants, 20, 6, 607-618.

3 R. Kovivikko, S. Pastorelli, A. Rodriguez-Bernaldo de Quiros, R. Paseiro-Cerrato, P. Paseiro-Losada, C. Simoneau. Rapid multi-analyte quantification of benzophenone, 4-methylbenzophenone and related derivatives from paperboard food packaging (2010) Food Additives and Contaminants, 27, 10, 1478-1486.

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