



**HAL**  
open science

## Furan determination in jarred baby food purchased from the Spanish market by headspace gas chromatography-mass spectrometry.

Elvira Ruiz

► **To cite this version:**

Elvira Ruiz. Furan determination in jarred baby food purchased from the Spanish market by headspace gas chromatography-mass spectrometry.. *Food Additives and Contaminants*, 2010, 27 (09), pp.1208-1214. 10.1080/19440049.2010.489578 . hal-00602981

**HAL Id: hal-00602981**

**<https://hal.science/hal-00602981>**

Submitted on 24 Jun 2011

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



**Furan determination in jarred baby food purchased from the Spanish market by headspace gas chromatography-mass spectrometry.**

Journal:	<i>Food Additives and Contaminants</i>
Manuscript ID:	TFAC-2010-049.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	20-Apr-2010
Complete List of Authors:	Ruiz, Elvira; Spanish Food Safety and Nutrition Agency, Food Contact Materials Section, National Food and Nutrition Centre
Methods/Techniques:	Chromatography - GC/MS, Chromatography - Headspace
Additives/Contaminants:	Process contaminants
Food Types:	Baby food

SCHOLARONE™  
Manuscripts

## Furan determination in jarred baby food purchased from the Spanish market by headspace gas chromatography-mass spectrometry

Elvira Ruiz\*, Ma Isabel Santillana, Ma Teresa Nieto, Ma Eugenia Cirugeda, and Jose J. Sánchez

*Food Contact Materials Section, National Food Centre, Spanish Food Safety and Nutrition Agency, Majadahonda, 28220 Madrid, Spain*

\*Corresponding author. Email: eruizm@msps.es

### Abstract

The aim of this paper is to offer a method based on headspace gas chromatography-mass spectrometry technique (US FDA 2006) in-house validated and use to estimate furan concentrations in jarred baby food samples purchased from the Spanish market. The validation was performed according to ISO 17025 and EFSA requirements and the results obtained (LOD 0.05  $\mu\text{g.kg}^{-1}$ ; LOQ 4  $\mu\text{g.kg}^{-1}$ , lowest validated level; RSD% 3.1-10.5; recoveries 85.4-101.5%) confirm that this method is fit for the routine analysis of furan in jarred baby food control. Furan was analysed in 39 different baby-food samples and the mean levels varied between 64.6  $\mu\text{g.kg}^{-1}$  (rice and chicken samples) and  $\leq$  LOQ (fruit-based samples). The mean concentration values found for the different matrices were 5.0, 37.8, 25.2, 33.8 and 30.5  $\mu\text{g.kg}^{-1}$  for fruit, vegetables, meat/vegetables, fish/vegetables and dairy-containing baby foods, respectively. According to the statistical analyses, fruit-based baby food samples had significantly lower concentrations of furan. Mean values for the other matrices were at least five times higher, and this is in accordance with the levels reported in other studies.

**Keywords:** furan; baby-food; headspace-gas chromatography-mass spectrometry.

## Introduction

Furan is a lipophilic contaminant which is formed during the heating processes used for the manufacture of foods. It is an aromatic heterocyclic compound, highly volatile; which was already detected, although at low concentration levels in the 1960s in a great variety of heat-processed foods (canned meat, bread, coffee, hydrolyzed proteins...) (Stoffelsma et al., 1968; Persson et al., 1973).

Experimental models multiple precursors and alternative routes for the furan formation have been proposed: thermal oxidation of ascorbic acid, non-enzimatic browning involving reducing sugars only (Strecker degradation) or together with amino acids [Maillard reactions (Maga 1979), polyunsaturated fat acids oxidation (Locas et al., 2004; Becalski et al., 2005; Märk et al., 2006)].

In 2004 US Food and Drug Administration (US FDA 2004b) reported the presence of this compound in a great variety of thermally treated food, such as meat, vegetables, and fruits, canned sauces in tins or jars especially including baby-food. The presence of furan, classified as possibly carcinogenic to human (Group 2B) (IARC 1995) in food has been confirmed by different laboratories (Reinhard et al., 2004; Becalski et al., 2005; Heppner et al., 2007)

The scientific panel on contaminants in the food chain from the European Food Safety Authority (EFSA 2004) considered furan in foodstuff as an urgent matter and made a scientific report about its presence that was presented in Brussels. The report concluded that it was necessary to generate reliable data of the furan content in products commercialized within the European Community to create a good database and study the risk of furan toxicity. In 2007, the European Commission recommended to the members states to follow the presence of furan in thermally treated food throughout 2007-2008 (EC 2007).

As an answer to the Commission and EFSA recommendation, our laboratory taking into account the lack of data available in Spain, decided to carry out a market surveillance targeted on foods intended to be consumed by infants, since they are the most susceptible consumer group (Suk et al., 2003) and because relatively high amounts of furan were previously detected in commercial baby-food (Crews et al., 2007; Morehouse et al., 2008).

The determination of furan is very challenging due to its high volatility, low molecular weight, and its presence in low concentrations in foodstuff. It is very important to have a suitable method to analyze this compound. The most used analytical technique is

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

headspace extraction combined with gas chromatography-mass spectrometric determination (Nyman et al., 2006; Nyman et al., 2008; Bianchi et al., 2006; Zoller et al., 2007; Vranová et al., 2007). Our laboratory used the method proposed by FDA (US FDA 2006) as reference, with slight modifications.

The sample (purification was not necessary) was weighted in a headspace vial and placed in the static headspace autosampler, heated at 80° C for 30 min and determined by CG-MS in SIM mode, using furan-d4 as an internal standard.

## Experimental

### *Reagents and apparatus*

Furan (purity  $\geq 99\%$ ) and d<sub>4</sub>-Furan (isotopic purity  $\geq 98\%$ ) were provided by Sigma-Aldrich. Methanol (HPLC grade) from Merck. Ultrapure water was prepared using a Direct-Q system (Millipore).

The following equipment was used: Gas chromatograph (6890 Agilent) equipped with a mass spectrometer (5973 Agilent) and a Headspace injector (7694 Agilent). The chromatographic capillary column was a HP-PLOT Q by J&W Scientific (15 m x 0,32 mm x 20  $\mu\text{m}$ ).

20 ml headspace vials with PTFE septa (Agilent Technologies) were used. To prevent the presence of contaminants in the vials, they were heated in a muffle oven (Heraeus) at 400° C for 1 hour before being used.

The stock solutions were prepared and transferred using microsyringes (Hamilton Gastight®).

### *Standards preparation*

Stock furan and d<sub>4</sub>-furan solutions were prepared in methanol with a minimum concentration of 3000 mg.l<sup>-1</sup> and stored in a freezer for no longer than one week.

From the stock solutions, intermediate solutions of furan and d<sub>4</sub>-furan were prepared (50  $\mu\text{l}$  to 50 ml methanol) and from these, working solutions in water in the in the range 4 - 400  $\mu\text{g.l}^{-1}$  for furan and at 10  $\mu\text{g.l}^{-1}$  for d<sub>4</sub>-furan, approximately. The precise concentrations were calculated from the stock solutions. All these processes were performed in an ice bath to avoid losses due to the volatilization of furan.

### *Commercial samples for the study*

Thirty nine jarred baby food samples, corresponding to three different commercial brands, and including a wide range of different matrices were purchased in retail food

1  
2  
3 stores of the Spanish market. The samples were stored unopened and refrigerated, until  
4 they were analyzed. The main ingredients of the samples analyzed are shown in Table 2.  
5  
6  
7

### 8 **Sample preparation**

9  
10 A 5 g aliquot of the homogenised sample (homogenisation was performed under cold  
11 conditions) was weighted in a headspace vial, diluted with 5 ml of purified water and the  
12 internal standard was added at the same concentration as used in the calibration curve. All  
13 these processes were performed in an ice bath. The vials were hermetically sealed as fast  
14 as possible to avoid analyte losses and were shaken for 1 min until a homogeneous  
15 aspect was obtained. All the samples were twice analyzed, following the procedure  
16 already described. Additionally, a triplicate for each sample was prepared spiked with  
17 furan at a concentration of  $100 \mu\text{g.l}^{-1}$  in order to be used as a quality control sample.  
18  
19  
20  
21  
22  
23  
24

### 25 **HS-GC-MS analysis**

26  
27 Gas chromatographic conditions as well as (split ratio of 1:10) MS conditions were the  
28 same as those described in the US FDA 2006 method. The headspace operating  
29 conditions were as follows: oven temperature at  $80^{\circ}\text{C}$  with an equilibrium time of 30 min  
30 (stirring), loop at  $95^{\circ}\text{C}$ , transfer line at  $110^{\circ}\text{C}$  and an injection time of 1 min.  
31  
32  
33

34 Selected ion monitoring (SIM), ions  $m/z$  68, 39 (furan), 72 (furan  $d_4$ ). Chromatograms  
35 for furan and  $d_4$ -furan standards and for a baby food sample are presented in figure 1.  
36  
37  
38  
39

40 (Figure 1)

### 41 **Validation**

42  
43 In-house validation was carried out following the standard protocol from our laboratory,  
44 which is based on ISO 17025 (2005). The following parameters were assessed: specificity,  
45 linearity, detection and quantification limits, precision and accuracy (expressed as  
46 recovery).  
47  
48  
49

50 Specificity was tested verifying the lack of response at the retention time of the analyte  
51 by analysing in triplicate a blank sample. A response was considered to be present if it  
52 was  $\geq 1/5$  the value of the quantification limit.  
53  
54  
55

56 Linear regression calibration was performed by plotting the relative response of furan  
57 ( $m/z$  68) and  $d_4$ -furan ( $m/z$  72) against the furan concentration in  $\mu\text{g.l}^{-1}$ . An average  
58 calibration curve was calculated from three curves obtained in different days, each one at  
59 six concentration levels in the range 4 to  $400 \mu\text{g.l}^{-1}$ . Linearity was established by  
60

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

estimating the relative standard deviation of the mean slope, according to the following equation:

$$Cm \% = 100 \times \frac{Sm}{m}$$

Where  $Sm$  is the standard deviation of the mean slope and  $m$  is the slope of the mean calibration curve. Values of  $Cm \leq 5 \%$  are considered satisfactory. The correlation coefficient of the linear regression was also calculated ( $\geq 0.996$ ).

Limits of quantification ( $LOQ$ ) and detection ( $LOD$ ) were calculated from the mean calibration curve using the following equations:

$$LOQ = \frac{10 \times S_b}{m\sqrt{n}}$$

$$LOD = \frac{3 \times S_b}{m\sqrt{n}}$$

Where  $S_b$  is the intercept standard deviation,  $m$  is the slope of the mean calibration curve and  $n$  is the number of calibration curves.

Precision and accuracy were assessed spiking a blank sample with furan at three different levels of concentration (Table 1) Each level was analyzed three times on three different days ( $n = 9$ ). Precision was expressed in terms of relative standard deviation ( $RSD\% \leq 20$ ) and the accuracy as percentage of recovery for each concentration level (80 -120 %).

## Results and discussion

Previous to method validation, some experiments were performed using different headspace incubation temperatures, in order to evaluate the influence on the furan response. These temperatures were: 60° C, as recommended in the FDA method, and 80°C which is the temperature we have previously used in our laboratory for other volatile compounds, and also used by other authors (Nyman et al., 2006; Zoller et al., 2007; Morehouse et al., 2008).

To check the effect of the temperature, we obtained calibration curves prepared on different matrices: water, fruit juice and vegetable purée, at both temperatures. The slopes



1  
2  
3 of the regression lines, including all the matrices as well as both temperatures were  
4 compared. No significant difference was found between the mean slope obtained at 60°C  
5 (n=3) and at 80°C (n=4), (t test,  $\alpha=0.05$ ). Therefore, we concluded that setting the  
6 headspace temperature at 80°C would not lead to a significant increase of the furan  
7 concentration in the samples within the scope of our study.  
8  
9

10  
11 The in-house validation was performed as it has been described using a fruit based  
12 baby-food sample, where the absence of furan had been previously checked ( $<1/5$  LOQ),  
13 which was taken as the blank sample.  
14  
15

16  
17 The mean calibration curve (of three curves obtained on three days) with a furan  
18 concentration range 4 to 400  $\mu\text{g.l}^{-1}$  (equivalent to  $\mu\text{g.kg}^{-1}$  sample) showed a good linearity  
19 ( $C_m\% = 0.25$ ) and the correlation coefficient was 0.9999.  
20  
21

22  
23 Detection and quantification limits were calculated from the intercept value:  $0.05 \mu\text{g.kg}^{-1}$   
24 and  $0.17 \mu\text{g.kg}^{-1}$ , respectively. The lowest validated concentration level was  $4 \mu\text{g.kg}^{-1}$ , and  
25 this was considered as the quantification limit for the report of sample results.  
26

27  
28 Precision (RSD %) and accuracy (% recovery) results are presented in Table 1. Both  
29 parameters were satisfactory according to our internal requirements.  
30  
31

32  
33 (Table 1)  
34  
35

36  
37 Therefore, method performance parameters assessed in the method validation showed  
38 that the analytical procedure was well applicable for the reliable determination of furan in  
39 baby food with a limit of quantification suitable for the purpose of our study. Furthermore,  
40 the validation results fulfil EFSA requirements (EFSA 2007): quantification limit less than 5  
41  $\mu\text{g.kg}^{-1}$ , precision (as RSD %) less than 20% and a minimum recovery of 80%. Also, the  
42 suitability of the method was confirmed by participating in an inter-laboratory trial  
43 (FAPAS®) on a vegetable based baby-food. The z-score obtained was 0.4, which was in  
44 the range of  $\leq \pm 2$ , considered as satisfactory.  
45  
46  
47  
48  
49

50  
51 The method was applied to the analysis of the jarred baby food samples described in  
52 Table 2. All the samples were analyzed twice and a parallel recovery analysis was done  
53 for all of them. The results are shown in Table 2.  
54  
55  
56

57  
58 (Table 2)  
59  
60



1  
2  
3 When the baby-food data were processed, precision data of duplicate analysis satisfied  
4 the Thompson modified Horwitz equation (Thompson 2000). This is equivalent to a  
5  $\text{HorRat}_r \leq 1$ .  
6  
7

8 The average recovery value was 101.5% with a relative standard deviation  $\text{RSD}\% =$   
9 5.6, which is in complete agreement with the results obtained in the method validation.  
10

11 The thirty-nine baby-food samples analyzed by the method previously described were  
12 classified depending on their composition (most common ingredients) in five different  
13 groups. Table 3 summarizes the mean value per group as well as the maximum and  
14 minimum found values.  
15  
16  
17

18  
19  
20 (Table 3)  
21  
22  
23

24 From Table 3 it is evident that fruit-based baby food showed the lowest furan  
25 concentrations ( $5 \mu\text{g}\cdot\text{kg}^{-1}$ ) and the highest values were found in the meat (chicken, turkey  
26 and seabass) and vegetables group (62 to  $65 \mu\text{g}\cdot\text{kg}^{-1}$ ). Due to the limited number of  
27 analyzed samples based only on vegetables and dairy products ( $n=4$ ), the results for these  
28 groups might not be representative and have to be carefully considered.  
29  
30  
31

32 Furan concentrations in baby food samples from the Spanish market included in our  
33 study are in agreement with the levels determined in other studies (Bekalsi et al., 2005;  
34 Bianchi et al., 2006; Morehouse et al., 2008; Zoller et al., 2007); neither are they in  
35 disagreement with those included in the EFSA database where concentration levels  
36 ranged from not detectable to  $112 \mu\text{g}\cdot\text{kg}^{-1}$  (EFSA 2004). In our study the levels found were  
37 from  $<\text{LOQ}$  up to  $65 \mu\text{g}\cdot\text{kg}^{-1}$ .  
38  
39  
40  
41  
42

43 All samples analysed were commercial baby foods prepared by autoclaving in glass  
44 jars, technology which has been suggested to favor furan formation over other procedures  
45 used for commercial baby food preparation and domestic practices (Roberts et al., 2008;  
46 US FDA, 2004a; Zoller et al., 2007).  
47  
48  
49

50 It must be noticed that fruit based products with added ascorbic acid contain also  
51 organic acids. It has been reported that the formation of furan from sugars or ascorbic acid  
52 is less likely at low pH (Becalski et al., 2005; Limacher et al., 2007). Apparently, the  
53 preparation of autoclaved baby foods does not include processing conditions of low water  
54 activity at high temperatures typical for non-enzymatic browning reactions to occur; thus  
55 furan is more likely formed through other mechanisms (Maillard reaction). It is possible to  
56 speculate that most potential precursors for furan in such baby food are polyunsaturated  
57  
58  
59  
60

1  
2  
3 lipids such as polyunsaturated fatty acids and carotenoids (Becalski et al., 2005; Locas et  
4 al., 2004). However; this was not the purpose of our study

5  
6 The composition of baby food seems to be a key factor to be taken into account in furan  
7 formation (presence of ascorbic acid, polyunsaturated fatty acids, aminoacids and  
8 carotenoids), as has already been described in previous studies regarding this analyte  
9 (Jestoi et al., 2009; Lachenmeier et al., 2009).  
10  
11  
12

### 13 14 15 **Acknowledgements**

16 The authors would like to thank Juana Bustos and Marta Tello for technical assistance and  
17 critical reading of the manuscript.  
18  
19  
20

### 21 22 23 **References**

24  
25  
26  
27 Bianchi F, Careri M, Mangia A, Musci M. 2006. Development and validation of a solid  
28 phase micro-extraction-gas chromatography-mass spectrometry method for the  
29 determination of furan in baby-food. *Journal of Chromatography A*, 1102:268-272.  
30  
31  
32

33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
66  
67  
68  
69  
70  
71  
72  
73  
74  
75  
76  
77  
78  
79  
80  
81  
82  
83  
84  
85  
86  
87  
88  
89  
90  
91  
92  
93  
94  
95  
96  
97  
98  
99  
100  
101  
102  
103  
104  
105  
106  
107  
108  
109  
110  
111  
112  
113  
114  
115  
116  
117  
118  
119  
120  
121  
122  
123  
124  
125  
126  
127  
128  
129  
130  
131  
132  
133  
134  
135  
136  
137  
138  
139  
140  
141  
142  
143  
144  
145  
146  
147  
148  
149  
150  
151  
152  
153  
154  
155  
156  
157  
158  
159  
160  
161  
162  
163  
164  
165  
166  
167  
168  
169  
170  
171  
172  
173  
174  
175  
176  
177  
178  
179  
180  
181  
182  
183  
184  
185  
186  
187  
188  
189  
190  
191  
192  
193  
194  
195  
196  
197  
198  
199  
200  
201  
202  
203  
204  
205  
206  
207  
208  
209  
210  
211  
212  
213  
214  
215  
216  
217  
218  
219  
220  
221  
222  
223  
224  
225  
226  
227  
228  
229  
230  
231  
232  
233  
234  
235  
236  
237  
238  
239  
240  
241  
242  
243  
244  
245  
246  
247  
248  
249  
250  
251  
252  
253  
254  
255  
256  
257  
258  
259  
260  
261  
262  
263  
264  
265  
266  
267  
268  
269  
270  
271  
272  
273  
274  
275  
276  
277  
278  
279  
280  
281  
282  
283  
284  
285  
286  
287  
288  
289  
290  
291  
292  
293  
294  
295  
296  
297  
298  
299  
300  
301  
302  
303  
304  
305  
306  
307  
308  
309  
310  
311  
312  
313  
314  
315  
316  
317  
318  
319  
320  
321  
322  
323  
324  
325  
326  
327  
328  
329  
330  
331  
332  
333  
334  
335  
336  
337  
338  
339  
340  
341  
342  
343  
344  
345  
346  
347  
348  
349  
350  
351  
352  
353  
354  
355  
356  
357  
358  
359  
360  
361  
362  
363  
364  
365  
366  
367  
368  
369  
370  
371  
372  
373  
374  
375  
376  
377  
378  
379  
380  
381  
382  
383  
384  
385  
386  
387  
388  
389  
390  
391  
392  
393  
394  
395  
396  
397  
398  
399  
400  
401  
402  
403  
404  
405  
406  
407  
408  
409  
410  
411  
412  
413  
414  
415  
416  
417  
418  
419  
420  
421  
422  
423  
424  
425  
426  
427  
428  
429  
430  
431  
432  
433  
434  
435  
436  
437  
438  
439  
440  
441  
442  
443  
444  
445  
446  
447  
448  
449  
450  
451  
452  
453  
454  
455  
456  
457  
458  
459  
460  
461  
462  
463  
464  
465  
466  
467  
468  
469  
470  
471  
472  
473  
474  
475  
476  
477  
478  
479  
480  
481  
482  
483  
484  
485  
486  
487  
488  
489  
490  
491  
492  
493  
494  
495  
496  
497  
498  
499  
500  
501  
502  
503  
504  
505  
506  
507  
508  
509  
510  
511  
512  
513  
514  
515  
516  
517  
518  
519  
520  
521  
522  
523  
524  
525  
526  
527  
528  
529  
530  
531  
532  
533  
534  
535  
536  
537  
538  
539  
540  
541  
542  
543  
544  
545  
546  
547  
548  
549  
550  
551  
552  
553  
554  
555  
556  
557  
558  
559  
560  
561  
562  
563  
564  
565  
566  
567  
568  
569  
570  
571  
572  
573  
574  
575  
576  
577  
578  
579  
580  
581  
582  
583  
584  
585  
586  
587  
588  
589  
590  
591  
592  
593  
594  
595  
596  
597  
598  
599  
600  
601  
602  
603  
604  
605  
606  
607  
608  
609  
610  
611  
612  
613  
614  
615  
616  
617  
618  
619  
620  
621  
622  
623  
624  
625  
626  
627  
628  
629  
630  
631  
632  
633  
634  
635  
636  
637  
638  
639  
640  
641  
642  
643  
644  
645  
646  
647  
648  
649  
650  
651  
652  
653  
654  
655  
656  
657  
658  
659  
660  
661  
662  
663  
664  
665  
666  
667  
668  
669  
670  
671  
672  
673  
674  
675  
676  
677  
678  
679  
680  
681  
682  
683  
684  
685  
686  
687  
688  
689  
690  
691  
692  
693  
694  
695  
696  
697  
698  
699  
700  
701  
702  
703  
704  
705  
706  
707  
708  
709  
710  
711  
712  
713  
714  
715  
716  
717  
718  
719  
720  
721  
722  
723  
724  
725  
726  
727  
728  
729  
730  
731  
732  
733  
734  
735  
736  
737  
738  
739  
740  
741  
742  
743  
744  
745  
746  
747  
748  
749  
750  
751  
752  
753  
754  
755  
756  
757  
758  
759  
760  
761  
762  
763  
764  
765  
766  
767  
768  
769  
770  
771  
772  
773  
774  
775  
776  
777  
778  
779  
780  
781  
782  
783  
784  
785  
786  
787  
788  
789  
790  
791  
792  
793  
794  
795  
796  
797  
798  
799  
800  
801  
802  
803  
804  
805  
806  
807  
808  
809  
810  
811  
812  
813  
814  
815  
816  
817  
818  
819  
820  
821  
822  
823  
824  
825  
826  
827  
828  
829  
830  
831  
832  
833  
834  
835  
836  
837  
838  
839  
840  
841  
842  
843  
844  
845  
846  
847  
848  
849  
850  
851  
852  
853  
854  
855  
856  
857  
858  
859  
860  
861  
862  
863  
864  
865  
866  
867  
868  
869  
870  
871  
872  
873  
874  
875  
876  
877  
878  
879  
880  
881  
882  
883  
884  
885  
886  
887  
888  
889  
890  
891  
892  
893  
894  
895  
896  
897  
898  
899  
900  
901  
902  
903  
904  
905  
906  
907  
908  
909  
910  
911  
912  
913  
914  
915  
916  
917  
918  
919  
920  
921  
922  
923  
924  
925  
926  
927  
928  
929  
930  
931  
932  
933  
934  
935  
936  
937  
938  
939  
940  
941  
942  
943  
944  
945  
946  
947  
948  
949  
950  
951  
952  
953  
954  
955  
956  
957  
958  
959  
960  
961  
962  
963  
964  
965  
966  
967  
968  
969  
970  
971  
972  
973  
974  
975  
976  
977  
978  
979  
980  
981  
982  
983  
984  
985  
986  
987  
988  
989  
990  
991  
992  
993  
994  
995  
996  
997  
998  
999  
1000

Becalski A, Forsyth D, Casey V, Lau BP-Y, Pepper K, Seaman S. 2005. Development and validation of a headspace method for determination of furan in food. *Food Additives and Contaminants*, 22:535-540.

Becalski A, Seaman S. 2005. Furan precursors in food: A model study and development of a simple headspace method for determination of furan. *Journal AOAC International*, 88:102-106.

Crews C, Castle L. 2007. A review of the occurrence, formation and analysis of furan in heat-processed foods. *Trends in Food Science & Technology* 18:365-372.

European Food Safety Authority (EFSA). 2004. Report on the Scientific Panel on contaminants in the food chain on provisional findings on furan in food. *EFSA Journal*, 137:1-20.

European Food Safety Authority (EFSA). 2007. Criteria for accepting furan data Rev.1. *OJ L 88*, 29.3.2007, p.56.

1  
2  
3  
4 European Commission. 2007. Recommendation concerning the assessment of furan  
5 presence in food. 2007/196/EC  
6  
7

8  
9  
10 Heppner C.W, Schlater J R. 2007. Data requirements for risk assessment of furan in food.  
11 Food Additives and Contaminants, 24 (S1):114-121.  
12  
13

14  
15 International Agency for Research on Cancer (IARC). 1995. Dry cleaning, some  
16 chlorinated solvents and other industrial chemicals, monographs on the evaluation of  
17 carcinogenic risks to humans, vol 63:393-407.  
18  
19

20  
21  
22 Jestoi M, Jävinen T, Järvenpää E, Tapanainen H, Virtanen S, Peltonen K. 2009. Furan in  
23 the baby-food simples purchased from the Finnish markets. Determination with SPME-GC-  
24 MS. Food Chemistry, 117:522-528.  
25  
26

27  
28  
29 Lachenmeier DW, Reusch H, Kuballa T. 2009. Risk assessment of furan in commercially  
30 jarred baby foods, including insights into its occurrence and formation in freshly home-  
31 cooked foods for infants and young children. Food Additives and Contaminants, 26  
32 (6):776-785.  
33  
34

35  
36  
37  
38 Limacher A, Kerler J, Conde-Petit B, Blank I. 2007. Formation of furan and methylfuran  
39 from ascorbic acid in model systems and food. Food Additives and Contaminants, 24 (S1),  
40 122-135  
41  
42

43  
44  
45 Locas C, Yaylayan V.A. 2004. Origin and mechanistic pathways of formation of the parent  
46 furan: A toxicant. Journal of Agricultural Food Chemistry, 52:6830-36.  
47  
48

49  
50  
51 Maga J.A. 1979. Furan in foods. 1979. CRC Critical Reviews in Food Science and  
52 Nutrition, 11:355-400.  
53  
54

55  
56 Märk J, Pollien P, Lindinger C, Blank I, Märk T. 2006. Quantitation of furan and  
57 methylfuran formed in different precursor systems by proton transfer reaction mass  
58 spectrometry. Journal of Agricultural and Food Chemistry, 54:2786-2793.  
59  
60

1  
2  
3 Morehouse, KM, Nyman PJ, Mcneal TP, DiNovi MJ, Perfetti GA. 2008. Survey of furan in  
4 heat processed oods by headspace gas chromatography/mass spectrometry and estimate  
5 adult exposure. Food Additives and Contaminants, 25(3):259-264.  
6  
7

8  
9  
10 Nyman PJ, Morehouse KM, McNeal TP, Perfetti GA, Diachenko GW. 2006. Single-  
11 laboratory validation of a method for the determination of furan in foods by using static  
12 headspace sampling and gas chromatography/mass spectrometry. Journal of AOAC  
13 International, 89 (5):1417-1424.  
14  
15

16  
17  
18 Nyman PJ, Morehouse KM, McNeal TP, Perfetti GA, Diachenko GW, Holcomb JR. 2008.  
19 Single laboratory validation of a method for the determination of furan in foods by  
20 headspace gas chromatograph/ mass spectrometry, Part 2: Low-moisture snack foods. J.  
21 AOAC Int 91 (2): 414-421  
22  
23  
24

25  
26  
27 Persson T, Von Sydow E. 1973. Aroma of canned beef: Gas chromatographic and mass  
28 spectrometric analysis of the volatiles. Journal of Food Science, 38:377-385.  
29  
30

31  
32  
33 Reinhard H, Sager F, Zimmermann H, Zolter O. 2004. Furan in foods on the Swiss mark –  
34 method and results. Mitteilungen in Lebensmittel Hygiene, 95:532-535.  
35  
36

37  
38 Roberts D, Crews C, Grundy H, Mills C, Matthews W. 2008. Effect of consumer cooking on  
39 furan in convenience foods. Food Additives and Contaminants, 25 (1): 25-31  
40  
41

42  
43 Stoffelsma J, Sipma G, Kettenes DK, Pypker J. 1968. Volatile components or roasted  
44 coffee. Journal of Agricultural and Food Chemistry, 16:1000-1004.  
45  
46

47  
48 Suk WA, Murria K, Avakian MD. 2003. Environmental hazards to children's health in the  
49 modern Word. Mutat Res. 544:235-242.  
50  
51

52  
53  
54 Thompson M. 2000. Recent trends in interlaboratory precision at ppb and sub-ppb  
55 concentration in relation to fitness for purpose criteria in proficiency testing. Analyst, 125:  
56 385-386  
57  
58

59  
60  
UNE-EN ISO/IEC 17025. 2005. Requisitos generales para la competencia de los  
laboratorios de ensayo y calibración.

1  
2  
3  
4 US Food and Drug Administration (FDA). 2004b. Determination of furan in foods. 7 May  
5 2004(updated 27 October 2006). Available from: <http://www.cfsan.fda.gov/dms/furan.html>  
6  
7  
8

9  
10 Vranová J, Bednářiková A, Ciesarová Z. 2007. In-house validation of a simple headspace  
11 gas chromatography-mass spectrometry method for determination of furan levels in food.  
12 Journal of Food and Nutrition Research, 46 (3):123-127.  
13  
14

15  
16  
17 Zoller O, Sager F, Reinhard H. 2007. Furan in food: Headspace method and product  
18 survey. Food Additives and Contaminants, 24 (S1):91-107.  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

Table 1: Mean recoveries and relative standard deviations of furan determinations at three different spiking levels used. Each spiking level is represented by 9 replicates.

<b>n = 9</b>	<b>Level 1 (4 µg.kg<sup>-1</sup>)</b>	<b>Level 2 (115 µg.kg<sup>-1</sup>)</b>	<b>Level 3 (384 µg.kg<sup>-1</sup>)</b>
Mean recovery (%)	85.4	101.5	101.1
RSD (%)	10.5	3.1	4.0

For Peer Review Only

Table 2: The different jarred baby food samples analysed with the ingredients reported by the manufactures and furan mean concentration found.

Number	Brand	Product	Ingredients	Furan $\mu\text{g.kg}^{-1}$
1	A	Vegetables and Spanish veal	Water, potatoes, Spanish veal, beans, carrots, peas, celery and rice flour.	15.1
2	A	Multifruits	Peach, apple, banana, orange, water, sugar, rice flour and vitamin C.	NQ.*
3	A	Mixed vegetables	Potatoes, water, green beans, carrots, peas, onion, celery, tomato, sunflower oil, rice flour and salt.	53.4
4	A	Rice and chicken	Water, chicken, carrots, rice flour, corn starch, sunflower oil, onion, celery, tomato and salt.	NQ*
5	B	Carrots and veal	Water, veal, potatoes, carrots, rice, tomatoes, starch, sunflower oil, onion, celery and salt.	11.9
6	B	Turkey and vegetables	Water, turkey meat, potatoes, peas, tomato, rice, onion, starch, sunflower oil and salt.	12.8
7	B	Ham, veal and vegetables	Water, potatoes, ham, tomato, veal, carrots, rice, onion, starch, sunflower oil, salt and garlic.	10.4
8	B	Vegetable soup and lamb	Water, potatoes, lamb carrots, peas onion, starch, sunflower oil, salt, parsley and garlic.	21.3
9	B	Fruit cocktail	Pears, apples, bananas, oranges, water, sugar, rice flour and vitamin C.	NQ*
10	B	Vegetables soup and lamb	Water, potatoes, lamb, carrots, peas, onions, starch, sunflower oil, salt, parsley and garlic.	29.3
11	B	Chicken and rice	Water, chicken, rice, carrots, starch, tomato, sunflower oil, onion, celery y salt.	17.4
12	B	Chicken, veal and vegetables	Water, potatoes, green beans, chicken, tomato, carrots, peas, veal, starch, celery, sunflower oil, onion, sugar and salt.	28.8
13	B	Ham, veal and vegetables	Water potatoes, ham, tomato, veal, carrots, rice, onion, starch, sunflower oil, salt and garlic.	20.6
14	B	Veal and carrots	Water, veal, potatoes, carrots, rice, tomato, starch, sunflower oil, onion, celery and salt.	19.9
15	B	Rice and carrots in chicken soup	Chicken soup, carrots, chicken, rice, onion, corn starch, olive oil, vegetables oils, parsley, salt and bay leaves.	11.3
16	B	Rice and hake	Water, potatoes, hake, rice, onion, sunflower oil, celery and salt.	13.9
17	B	Sole and béchamel	Water, potatoes, skimmed milk, sole, tomato, butter, starch, onion, celery and salt.	34.2
18	B	Peas and ham	Water, peas, potatoes, milk, ham, onion, corn starch, olive oil, vegetables oils, salt and aroma.	15.8
19	B	Chicken and vegetables	Water, potatoes, carrots, milk, chicken meat, onions, corn starch, tomato, celery, olive oil, vegetable oil and salt.	22.8
20	B	Vegetables with hake in a cream	Water, milk, hake, rice, onion, sunflower oil, celery, starch and salt.	14.2
21	B	Veil with carrots with olive oil	Water, veil meat, potatoes, carrots, rice, tomato, corn starch, olive oil, vegetable oil, onion, celery, salt.	12.6
22	B	Apple compote rich in vitamin C	Apple, sugar, starch, lemon juice, cinnamon and vitamin C.	5.1
23	B	Banana, tangerine and pear rich in vitamin C	Banana, tangerine, pear, apple, carrots, sugar, starch, lemon juice and vitamin C.	5.2
24	B	Varied fruit	Peach, apple, banana, apricot, orange, grape, corn starch, rice and vitamin C.	4.4
25	B	Peach and banana	Peach, banana, grape, corn starch and rice and vitamin C.	4,8
26	B	Milk dessert with biscuits	Milk, sugar, water, biscuits and rice flour.	39.8
27	B	Lentil stew	Water, lentils, potatoes, veil meat, carrots, tomato, onion, sunflower oil, starch, salt and spices.	22.2
28	B	Crème Caramel	Milk, sugar, water, rice flour, starch and vanilla.	21.2



Number	Brand	Product	Ingredients	Furan $\mu\text{g.kg}^{-1}$
29	C	Cream of béchamel and vegetables with chicken	Milk, water, chicken, potato, carrot, corn starch, butter, leak and green beans.	43.9
30	C	Rice and veal	Water, potato, carrot, veil, rice, onion, tomato, olive oil, leak and corn starch.	37.2
31	C	Banana, apple, orange and cereals.	Banana, apple, flour, honey, orange, lemon and vitamin C.	NQ*
32	C	Béchamel sauce and hake	Water, milk, hake, rice flour, corn starch, butter, salt and nutmeg.	34.2
33	C	Chicken with vegetables	Potato, water, carrot, chicken meat, leak, peas, onion, olive oil, corn starch and salt.	42.8
34	C	Gluten and additive free varied fruit.	Orange, apple, pear, apricot, water, sugar, rice flour and vitamin C.	7.4
35	C	Gluten and additive free Six fruit dessert.	Apple, peach, apricot, banana, orange, pineapple, sugar, water, rice flour and vitamin C.	7.8
36	C	Banana, orange and biscuit.	Banana, orange, water, sugar, gluten free biscuits, rice flour, corn, lemon and vitamin C.	9.0
37	C	Gluten and additives free chicken and rice.	Water, milk, chicken, potato, carrot, rice, corn starch, olive oil and salt.	64.6
38	C	Vegetable puree and turkey. Dinner for little ones.	Water, carrots, potatoes, milk, turkey, onion, green beans, olive oil, corn starch and salt.	62.8
39	C	Vegetables and seabass.	Water, carrots, potato, seabass, milk, turkey, onion, peas, green beans, olive oil, leak, corn starch and salt.	62.2

\* NQ = Not quantifying, LOQ =  $4 \mu\text{g.kg}^{-1}$

Table 3: Mean and maximum-minimum values per group depending on their composition.

Baby food based on:	n	Mean value ( $\mu\text{g}\cdot\text{kg}^{-1}$ ) <sup>(1)</sup>	Maximum value- Minimum value ( $\mu\text{g}\cdot\text{kg}^{-1}$ )
Fruits	10	5.0	NQ – 9.0
Vegetables	2	37.8	22.2 – 53.4
Meat and vegetables	20	25.2	NQ – 64.6
Fish and vegetables	6	33.8	13.9 – 62.2
Dairy products	2	30.5	21.2 – 39.8

<sup>(1)</sup> To calculate the mean value we have taken value 2 (LOQ/2) for the Non Quantifying samples.

1  
2  
3 Equation (1):

$$4 \quad Cm\% = 100 \times \frac{Sm}{m}$$

7  
8 Equation (2):

$$9 \quad LOQ = \frac{10 \times S_b}{m\sqrt{n}}$$

12  
13 Equation (3):

$$14 \quad LOD = \frac{3 \times S_b}{m\sqrt{n}}$$

15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

For Peer Review Only

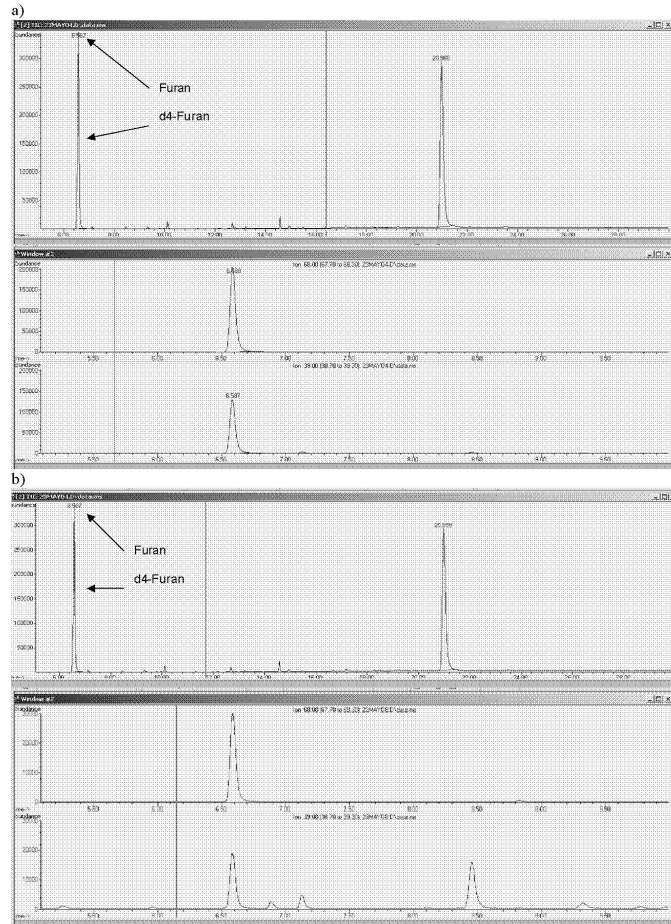


Figure 1. Typical HS-GC-MS SIM chromatogram and extracted single ions  $m/z$  68 and  $m/z$  39 of: a)  $98.6 \mu\text{g.kg}^{-1}$  furan standard and b) a meat and vegetables baby food sample ( $29.3 \mu\text{g.kg}^{-1}$ ).

210x297mm (200 x 200 DPI)