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Trace analysis of bisphenol A in canned food by DI-SPME-Arrow-GC-MS/MS

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Introduction

BPA is a monomer used in the production of food contact materials such as packagings, storage containers and epoxy resins used for the cans metal coating. Its known harmful effects on human health were re-evaluated by EFSA in 2023, which imposed a new extremely low TDI of 0.2 ng/kg body weight per day (20,000 times lower than the previous one).

It has also been estimated that the human dietary exposure to BPA is two to three orders of magnitude higher than the new TDI [1]. Monitoring the presence of BPA at low concentrations in food has therefore become a current analytical issue of great importance. A DI-SPME-ARROW-GC-MS/MS method has been developed for this purpose.

Method

Description:
The method involves the derivatisation of BPA with acetic anhydride directly in the 20 ml headspace vial in aqueous environment in presence of sodium acetate and the C13 isotope of bisphenol A as internal standard (Fig.1C and Fig.2B).
The extraction of the bisphenol A diacetate occurs with SPME-ARROW, which is both selective and highly sensitive. The desorbed analytes are measured with a GC/MS-MS Agilent 7010B GC/TQ, using the multiple reaction monitoring acquisition (Fig.3).

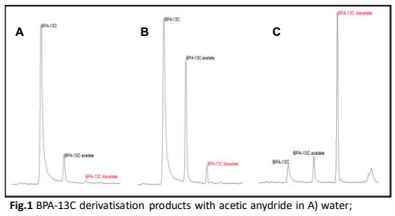


Fig.1 BPA-13C derivatisation products with acetic anydride in A) water; B) buffer solution pH 5; C) in sodium acetate 0,5M

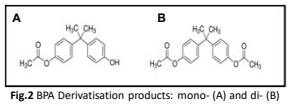


Fig.2 BPA Derivatisation products: mono- (A) and di- (B) acetate.

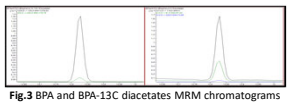
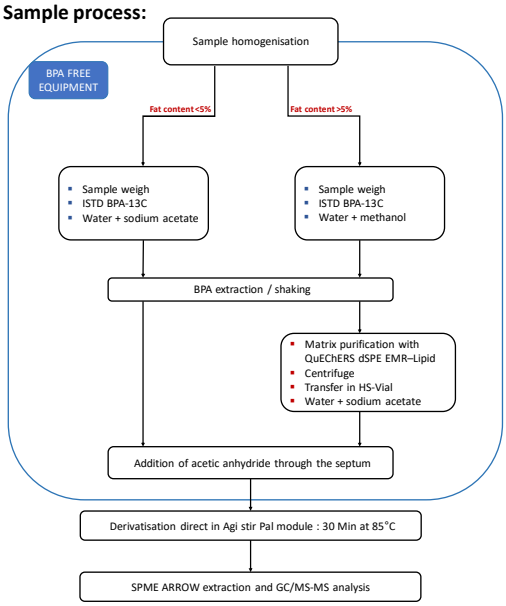


Fig.3 BPA and BPA-13C diacetates MRM chromatograms

Sample process:



SPME ARROW main topics:
Preservation of the phases structure and reduction of the background phenomena: PAL conditioning module, needle settings and rinsing procedures.

Agilent SPME	Out Diameter and thickness [2]	Incubation and extraction time	Bakeout settings	Rinsing solvent and time [2]
Polydimethylsiloxane (PDMS)	1.5 mm; 250 µm thickness	30 Min; 20 Min	270 °C; 7 Min	Ethanol; 2 Min.
Divinylbenzene/ Polydimethylsiloxane (DVB/PDMS)	1.1 mm; 120µm thickness	30 Min; 20 Min	250 °C; 5 Min	Methanol; 2 Min.
Polyacrylate (PA)	1.1 mm; 100 µm thickness	30 Min; 20 Min	250 °C; 5 Min	Hexan; 2 Min.

Tab.1 Tested SPME ARROWS and settings

Fig.4 MPS Robotic PAL

PAL3-SPME-ARROWCond
- Conditioning Temperatures and Time
- At a specific N_2 pressure of 2 bar (flow > 15mL/min)
- To avoid contamination in the GC inlet, cleaning the ARROW SPME after thermal desorption.
- To preserve the phases structure after immersion extraction.

Critical point between phase and rod. In this type of phase (PDMS) it is more visible than in others, but the damage effect is the same (see Fig.8 B)).

Fiber damage: not optimised settings for the pair of Vial penetration and needle penetration depth: Critical point is exposed during the immersion.

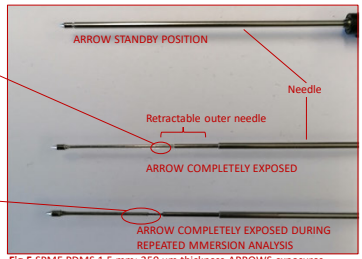


Fig.5 SPME PDMS 1.5 mm; 250 µm thickness ARROWS exposures

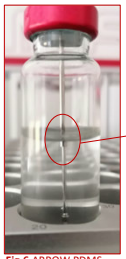


Fig.6 ARROW PDMS

Optimised SPME ARROW exposure during the immersion analysis step or rinsing step: trough the correct ratio of vial penatration to needle penetration depht, ensures that the critical point does not come into contact with the liquid extract, reducing the possibility of phase damage.

Results

Validation and samples results:
The validation of the method was performed on a carrot baby food in a glass jar with a BPA-free lid.

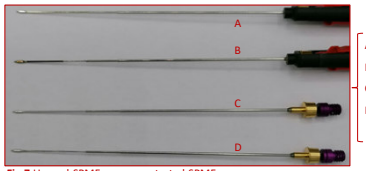
Validation parameters	r^2	Linear range ng/vial	LOQ ng/g	LOD ng/g	Precison (RDS%)
requiered	> 0,99	2 two orders of magnitude	< 1	< 0,5	< 20%
reached	0,9986	0,1 – 15	0,438	0,110	9,43

Tab.2 Validation data

/	Baby food carotte	Tomato sauce	Tomato paste
BPA (ppb) Resp. $ISTD_{STD}/ISTD_{SAMPLE}$	< LOD *1*	0,43 *1*	< LOD *1*
/	Mayonnaise	Salmon	Cocosnut milk
BPA (ppb) Resp. $ISTD_{STD}/ISTD_{SAMPLE}$	< LOQ *4*	< LOQ *2*	0,41 *1*

Tab.3 Results examples in different matrices

SPME outcomes:
All three tested SPME are sensitive and suitable for the trace analysis of BPA. The PDMS SPME ARROW (Fig.7) exhibited the greatest robustness.



A) PA SPME ARROW new (unused).
B) PA SPME ARROW after more than 50 vial extractions.
C) DVB/PDMS SPME ARROW new (unused).
D) DVB/PDMS SPME ARROW completely damaged after 50 extractions

Fig.7 Unused SPME arrows vs tested SPME arrows

Conclusion

The DI-SPME-ARROW-GC-MS/MS method, developed for the analysis of bisphenol A, has been demonstrated to be effective for a diverse range of food products. To ensure the consistent analysis of a large number of samples using the SPME ARROW phase, it is essential to implement sample purification procedures and to meticulously adjust the arrow phase settings for immersion in the vial extracts.

References
[1] https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2023.p210401
[2] https://www.agilent.com/cs/library/packageinsert/public/in-smart-spme-arrows-5994-3137en-agilent.pdf

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