Determination of Bisphenol A in water bottles by solid phase extraction by high performance liquid chromatography and tandem mass spectrometry

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Polycarbonate (PC) is a condensed polymer of bisphenol A (BPA) and carbonyl chloride or diphenyl carbonate and since it is clear, heat, microwave and impact resistant, it is used in the production of food containers such as baby tableware and water bottles. Several literature report the real danger of migration of BPA into foods. Because BPA exhibits estrogenic activity the 2004/19/EC Directive, that establishes a list of monomers and other starting substances which may be used for the manufacture of plastic materials and articles, reduces the specific migration limit for BPA (2002/72/EC) in food or food simulants from 3 to 0.6 mg/kg. The recent Commission Regulation (UE) 10/2011 on plastic materials and articles intended to come into contact with food, confirm the limit level, but the latest Implementing Regulation (UE/321/2011) totally forbids the use of BPA for the manufacture of infant feeding bottles. In this study, the presence of BPA in drinking water stocked in plastic bottles and dispenser was investigated using solid phase extraction procedure and LC-MS/MS analytical technique.

**LC-MS/MS setting**

- **Instrument**: Tandem Mass Spectrometer Quattro Micro™ API (Waters, Milliford, MA, USA) equipped with an electrospray ionization (ESI) source.
- **Operation mode**: multiple reaction monitoring (MRM) with negative ion mode.
- **Working conditions for ESI-MS/MS**: desolvation nitrogen gas flow, 250 l/h; cone gas (Ar) flow, 15 l/h; capillary voltage, 3.0 kV; ESI source temperature, 120°C; desolvation temperature, 250°C.
- **Optimization of parameters** of the LC-MS/MS method: direct infusion of a 1 µg/ml standard solution of BPA and 1 µg/ml of BPAd16 in methanol.

**Sample preparation**

For the extraction step, SPE Oasis® HLB columns were used, conditioned with 3 ml of methyl tert-butyl ether (MTBE), 3 ml of methanol and 3 ml of Milli-Q water. 500 ml of sample (acidified with 0.1 ml of formic acid until pH 3), added with 0.1 ml of internal standard BPAd16 (1000 ng/ml), were passed on the column (8 ml/min). After washing (3 ml of methanol 5% in water), BPA was eluted under gravity with 6 ml of methanol 10% in MTBE. The solvent was evaporated to dryness at 35°C. The sample was reconstituted, with acetonitrile/water (50/50 v/v) at pH 3, to a final volume of 1 ml and analysed by LC-MS/MS.

**HPLC method**

- **Instrument**: HPLC Alliance® 2695 (Waters, Milliford, MA, USA).
- **Reversed-phase column**: Discovery C18 (15.0 cm x 2.1 mm, 5 µm), Supelco, 30°C.
- **Mobile phase A**: H₂O Milli-Q.
- **Mobile phase B**: MeOH + 0.1% NH₃.
- **Flow rate**: 0.2 ml/min.
- **Run time**: 22 min.
- **Retention time BPA**: 11.3 min.
- **Injection volume**: 50 µl.
- **Autosampler**: 10°C.

**Samples results**

The method was used to analyse 14 samples: 8 drinking water stored in PC large volume dispenser, 4 in PET and 2 in glass with PVC top. All samples were compliant with the law limit, anyway all water contained in PC bottles were contaminated from 0.1 to 14.5 µg/kg. PC bottles analysed were close to the suggested expiry date.

**Conclusion**

The method investigated shows some advantages: 1) it is accurate, rapid, selective and sensitive; 2) satisfactory recoveries were obtained; 3) LC-MS/MS technique, using internal standard, allows an accurate analyte identification and quantification without signal suppression due to matrix effects; 4) the short run time of 22 minutes required allows the method to be applied in routine analysis; 5) it is suitable for water official control, thanks to the very low detection limit reached in compare with the Regulation permitted level.

Contamination found in water samples suggest that migration of BPA from PC is possible in water too. For a good human health, the water quantity suggested is about 2 litres per day, so, even if the BPA contamination found is really low, it would be better to eliminate the use of PC material for the manufacture of drinking water bottles, like was for infant feeding bottles (UE/321/2011) and to replace it with glass or PET.

![BPA spectrum: ionization and ionic fragmentation](image-url)

![Ion chromatogram of drinking water from PC bottle (14.5 µg/kg BPA)](image-url)