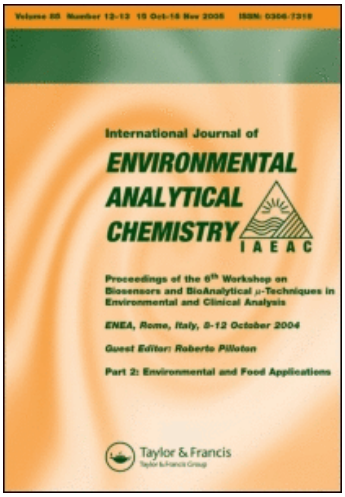

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Quantitative Determination of Bisphenol-A in River Water by Cool On-Column Injection-Gas Chromatography-Mass Spectrometry

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QUANTITATIVE DETERMINATION OF BISPHENOL-A IN RIVER WATER BY COOL ON-COLUMN INJECTION-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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A sensitive and selective method is described for the simultaneous quantitation and confirmation of bisphenol-A (BPA) in river water to support a surface water analysis study. The method employs a cool-on-column injection, gas chromatographic separation and detection by electron impact mass spectrometry (COC-GC-MS). River water samples (40 mL) were fortified with a stable isotope internal standard, deuterium labeled analog of BPA (D_8-BPA). The sample was then extracted with toluene and the extract was concentrated (400×) prior to analysis by COC-GC-MS. The analysis involves detection of the M^+ ion and the $[M\text{-}CH_3]^+$ ion (base peak) with quantitation based on the $[M\text{-}CH_3]^+$ ion response. The quantitation limit, with confirmation, for BPA for this method was determined to be 1 μg BPA/L of river water. Confirmation of BPA was determined by monitoring the ratio of the M^+ ion to the $[M\text{-}CH_3]^+$ ion. Calibration curves for standard concentrations of 1 μg/L to 20 μg/L resulted in correlation coefficients (r^2) of 0.9981 to 0.9999. The extraction/concentration efficiency for this method was determined to be 81.5%. Relative recoveries of BPA from river water ranged from 84% to 113% with an overall average of 102% ± 7% (1 to 20 μg/L). This method was developed to support a surface water analysis study to determine the level of BPA in surface water at five sites which use BPA in a manufacturing process and was sponsored by the Bisphenol-A Task Group of The Society of the Plastics Industry, Inc.

Keywords: Bisphenol-A; Cool On-Column Injection; Stable Isotope; Internal Standard; Mass Spectrometry

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INTRODUCTION

Bisphenol-A (BPA, CAS 80-05-7) is widely used in industry for a variety of applications such as in the production of polycarbonate polymers and epoxy resins. In 1993 five U.S. facilities produced approximately 0.64 billion kg of BPA. That year, approximately 365 kg BPA was reported released into surface waters. This 365 kg of BPA yields low flow concentrations in rivers predicted to be less than 1 μg BPA/L water.[1] However, a 1987 study of the environmental fate of BPA in surface waters, under acclimated conditions, shows BPA being rapidly biodegraded with half-lives of 2.5 to 4 days.[2] The Society of the Plastics Industry, Inc. (SPI) was interested in further understanding the concentration and fate of BPA in the aquatic environment. An initial step in this process was to determine and confirm the presence of BPA in river water where treated waste streams from manufacturers are discharged. This data would give an indication of potential environmental exposures of BPA in these receiving streams at a single point in time. This particular study[3] involved sampling rivers from five U.S. sites (Ohio River in Haverhill, OH and Mt. Vernon, IN; Brazos River in Freeport, TX; Alabama river in Burkville, AL; Patrick's Bayou in Deer Park, TX) which manufacture or use BPA in a manufacturing process. The requirements for the analytical method was that it provide BPA sensitivity at the 1 μg/L level with simultaneous confirmation. This limit of quantitation (1 μg BPA/L water) was selected based on the chronic toxicity level of the most sensitive fresh water species (*Selanastrum capricornutum*) with a 96-hr chronic NOEC of 1170 μg/L.[4] This NOEC level was then divided by 10 and an additional 100 fold safety factor was applied, which yields the 1 μg BPA/L water detection limit. A more recent study shows the 21-d chronic flow-through NOEC for Daphnia magna to be >3146 μ/L.[5] An additional requirement was that the methodology be as simple and reliable as possible. This would allow other laboratories who routinely conduct water quality testing to reproduce this method.

A review of some current methodology[6, 7] to quantitate and confirm BPA indicates the use of HPLC with fluorescence detection would provide the best opportunity to obtain the desired detection limit with some level of selectivity. However, modification of this methodology to determine BPA in surface water would require large volumes of sample to be manipulated to achieve the desired sensitivity and a separate analysis by mass spectrometry to obtain structural confirmation.

The BPA molecule possesses polar characteristics that make it difficult to achieve high quality capillary gas chromatography. This characteristic ultimately effects the detection limit which can be achieved in a given matrix. However, the

di-hydroxy functionality of BPA lends itself to chemical derivatization techniques that substantially improve the chromatographic properties and in turn the detection limit capabilities.[8, 9] This laboratory previously developed a chemical derivatization GC-NCI-MS method to quantitate BPA at the low μg/L level in biological matrices.[10] In contrast, this river water study would involve very diverse and undefined aqueous matrices. Again, the objective of this laboratory was to develop a simple and rugged analytical method that would allow the simultaneous quantitation and confirmation of 1 μg BPA/L of water. This paper describes the development and application of a cool on-column injection GC-MS method that meets this objective.

MATERIALS

Bisphenol-A (BPA) CAS 80-05-7 was obtained from The Dow Chemical Company (Freeport, Texas). D_8-BPA was obtained from Cambridge Isotope Laboratories (Andover, Massachusetts). ^{14}C-BPA was obtained from Wizard Laboratories (Davis, CA). Bisphenol-A low molecular weight oligomers (BPA-LMO) CAS 24936-68-3 was received from GE Corporate R&D (Schenectady, NY), Bis-GMA CAS 24447-72-1 was received from Polysciences Incorporated, (Warrington, PA). Bisphenol-A bis (chloroformate) (BPA-CIF) lot 03606DF, Bisphenol-A Dimethacrylate (BPA-DMA) lot 06430DG, and Poly (Bisphenol-A co-epichlorohydrin) (BADGE) lot 15227DN were obtained from Aldrich chemical Company (Milwaukee, WI). Deionized water from a Millipore water purification system (Millipore Corporation, Bedford, MA). All other reagents and solvents were reagent grade or better.

METHODS

BPA By HPLC-Fluorescence

The high performance liquid chromatography (HPLC) with fluorescence detection methodology was evaluated for use in determining BPA in river water. Standards of BPA in deionized and river (Patrick's Bayou) water were prepared at 99, 13, and 3 μg/L. These standards were injected (100 uL) by a Waters 717 (Millipore Corporation, Bedford, MA) plus autosampler onto a Waters u-Bondapak C_{18}, 3.9 $\times$ 300 mm column and eluted with an isocratic flow of 65% methanol in water at a flow rate of 1 cc/min delivered by a Hitachi L-6200A pump (Hitachi Ltd., Tokyo, Japan). Detection was accomplished using a Perkin Elmer LS-4 fluorescence spectrometer (Perkin Elmer Corporation, Norwalk, CT)

with an excitation slit of 15 nm and excitation wavelength of 230 nm, and an emission slit of 20 nm and emission wavelength of 308 nm.

BPA Analog Thermal Stability

The stability of representative BPA analogs was evaluated using three separate experiments. Five compounds were tested for thermal stability; Bisphenol-A low molecular weight oligomers (BPA-LMO), Bisphenol-A bis (chloroformate) (BPA-CIF), Bisphenol-A Dimethacrylate (BPA-DMA), Bis-GMA (BPA-GMA) and Poly (Bisphenol-A co-epichlorohydrin) (BADGE). In the first experiment each compound was diluted in toluene to a concentration of ~10 mg/L. A comparison stock solution of ~10 mg/L BPA in toluene was also prepared. These stock solutions were analyzed for BPA using GC-MS with an injection port temperature of 310°C which produced the best BPA peak shape. Thermal stability was based on the level of BPA detected in the BPA derivative samples expressed as a percentage of the BPA comparison stock solution. A second experiment consisted of analyzing the stock solution again for BPA using GC-MS. However, in the second analysis a cool on-column (COC) injection technique was employed. The third experiment consisted of preparing duplicate water samples of each BPA analog (and BPA comparison sample) at a concentration of 250 μg/L. These samples were taken through the complete sample preparation (extraction and concentration) and analysis procedure. This produced final concentrations of ~10 mg/L for each compound.

Water and Fortified Water Sample Preparation

River water samples were prepared for analysis as follows. A 40-mL aliquot of the sample was placed in a 50-mL glass vial. The samples were then fortified with (3 to 5 μL) of an internal standard solution prepared in acetonitrile which would yield D_8-BPA concentrations of ~10 to ~100 μg/L. The samples were extracted with duplicate 5 mL aliquots of toluene by vortex mixing for 5 minutes, followed by centrifugation for 6-10 minutes at 500 × g. The organic layers were combined from each extraction into a 20 mL glass vial and the solvent was evaporated to dryness using a Speed-vac concentrator (Savant Instruments Inc., Farmingdale, NY) at room temperature. The residues were re-constituted in 500 μL of toluene to facilitate the transfer to limited-volume GC vials. The sample was again evaporated to dryness at room temperature using a Speed-vac concentrator or under a gentle stream of nitrogen gas and the residue was re-constituted to a final volume of 100 μL with toluene for analysis by COC-GC-MS. Some samples (field samples) were fortified at the sampling sites by the

sampling personnel. When this occurred this laboratory provided the appropriate materials and instructions to each location to minimize variability in this aspect of the study. A detailed treatment of the sampling portion of this study is presented in the final report.[3] Validation samples were prepared by fortifying 40-mL aliquots of deionized or control river water with 1 to 20 μg/L of BPA (2-15 uL of an acetonitrile stock solution), followed by sample preparation as described above.

Matrix Standard Preparation

For each sample set analyzed a fresh set of matrix standards were prepared. Matrix standards consisted of 40-mL aliquots of deionized water fortified with known amounts of BPA analyte and D_8-BPA internal standard to bracket the expected BPA levels in the samples or fortified samples. These standards followed the samples through the same preparation procedure stated above. In addition to the matrix standards, each sample set included solvent blanks, water controls, water fortified with BPA only (no internal standard), and water fortified with D_8-BPA only (no BPA analyte). These additional blanks, controls, and samples are used to ensure the integrity of the sample set as well as monitor and correct for isotopic crossover contributions between analyte and internal standard ion response.

BPA Stability

The stability of BPA was evaluated in control river water from three of the sampling sites in this study (Ohio River, Alabama River, and Patrick's Bayou) and in toluene extracts over 17 days. Nine replicates of river water per site were fortified at 10 μg BPA/L water and stored at 5°C. Toluene extracts from matrix standards fortified from 1 to 20 μg BPA/L water (and ~10 ug D_8-BPA/L water internal standard) were also stored at room temperature. Three replicate river water samples per site were prepared and analyzed on day 0, 4, and 17. The toluene extracts were also analyzed on day 17. A fresh set of matrix standards was prepared for each analysis and the relative recovery of BPA was calculated based on the level of BPA fortified on day 0.

Filter Efficiency

In some surface water matrices it may be necessary to filter suspended particles from the sample to ensure the measurement of BPA dissolved in the matrix rather than BPA absorbed onto particulates. To ensure that filtration would not remove

BPA from the surface water being tested, a filter recovery experiment was conducted. Triplicate 20-mL aliquots from each of the five sites tested in this study were fortified with a known amount of ^{14}C-BPA (~24000 dpm). Each fortified aliquot was filtered through a Whatman 13mm, 0.7 um GF/F filter and the amount of ^{14}C-BPA in the filtrate determined by liquid scintillation counting.

GC-MS Analyses

All GC-MS analyses were performed on a Hewlett-Packard 5989 mass spectrometer (Hewlett-Packard Co., Palo Alto, California) equipped with a Hewlett-Packard Model 5890 gas chromatograph, a cool on-column injector and a Model 7673A autosampler. Separations were achieved on a DB-5 capillary column (30 m, 0.25 mm i.d., 0.5 μm film thickness; J & W Scientific, Folsom, California).

Operating conditions for qualitative GC-MS conditions used to obtain a full scan EI mass spectrum of BPA and D_8-BPA were as follows: a 1-μL splitless injection for 0.2 minutes, helium carrier gas at 20 psig head pressure, column temperature programmed from 80°C (1 min initial hold) to 285°C at a rate of 10°C/min followed by a hold at 285°C for 3.5 min, and the injection port and transfer line were both maintained at 280°C. The mass spectrometer was operated in the electron impact mode with an electron energy of 70 eV, the electron multiplier was operated at 1200 V, and the instrument scanned from 50 to 500 amu at 1 scan/sec.

Operating conditions for quantitative COC-GC-MS analyses of BPA in river water samples were as above except that the instrument was operated in the selected ion monitoring mode, monitoring ions m/z 228 (M^+), 213 ($[M\text{-}CH_{3+}]^+$), 236 (M^+ of D_8-BPA) and 221 ($[M\text{-}CH_3]^+$ of D_8-BPA). Ions m/z 213 and 221 were monitored at dwell times of 0.1 sec/ion/scan and ions m/z 228 and 236 were monitored at dwell times of 0.05 sec/ion/scan. Quantitation of BPA was performed by calculating the peak area ratio of ions m/z 213 to 221. Confirmation was performed by calculating the peak area ratio of ions m/z 228 to 213. The electron multiplier was set to 2585 V. Also, as previously mentioned, a cool-on-column injection technique was used where the injection port temperature was initially set at 72°C. The configuration of the on-column injection port is shown in Figure 1. This configuration is used to facilitate automated (7673A autosampler with a Hamilton 701 ASN, 10-uL, 23s/26s syringe) on-column injections employing capillary columns with internal diameters less than 0.53 mm.

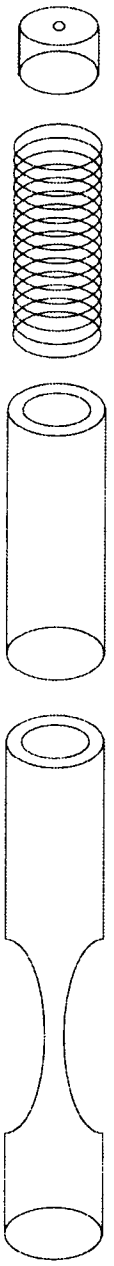

FIGURE 1 Cool On-Column Injection Port Configuration

Calculations

The quantitation of analytes may be complicated by isotopic crossover contributions to the ions of interest from BPA and D8-BPA since they co-elute from the GC column. Accurate quantitative data was obtained by correcting for these isotopic crossovers according to the method of Barbalas and Garland.[11]

RESULTS AND DISCUSSION

Method Development

Method development included the evaluation of HPLC/Fluorescence methodology. Figure 2 shows four HPLC/Fluorescence chromatograms of BPA in deionized and river (Patrick's Bayou) water. The river water chromatograms show interference peaks in the BPA retention time region which limits the detection limit to ~3 μg/L BPA in this particular river water matrix. After reviewing the above data and the method requirement that any BPA detected above the 1 μg/L level be structurally confirmed as BPA, modification of this methodology to include cleanup and/or concentration steps was not pursued by this laboratory. Additionally, the development of cleanup and concentration methodology for this particular river water matrix may not be applicable to other surface water matrices.

Method development experiments showed that heated injection port techniques caused two of the five representative BPA analogs to substantially thermally degrade to BPA (BPA-CIF at ~18% and BPA-LMO at ~80%) when compared to COC injection which showed thermal degradation levels at or below 2% for all the BPA analogs tested. This thermal degradation would produce false positives if the particular BPA analog was present in the water being analyzed for BPA. This method, therefore employed a cool-on-column injection technique to reduce the chance of thermal degradation of these and other possible BPA analogs to BPA during preparation and analysis. The number of BPA analogs that may be present in surface water and degrade to produce false positives for BPA is unknown and the five compounds tested in this study are not intended as a definitive list. These BPA analogs were chosen at random to investigate the potential for false positives and their selection was based on availability from commercial manufacturers. In addition, while conducting these experiments it was observed that one of the compounds tested (BPA-CIF), while showing no thermal degradation when a stock solution was directly analyzed using COC injection, produced false positives for BPA at the same level of thermal degradation (~18%) when a fortified water sample was taken through the entire

preparation and analysis method presented here. This data suggests that this particular compound (BPA-CIF) degraded in the sample preparation portion of the method. These thermal degradation experiments illustrate the importance of understanding the surface water matrix to be analyzed, the value of field fortified samples, and the value of an analytical method with the highest level of selectivity available.

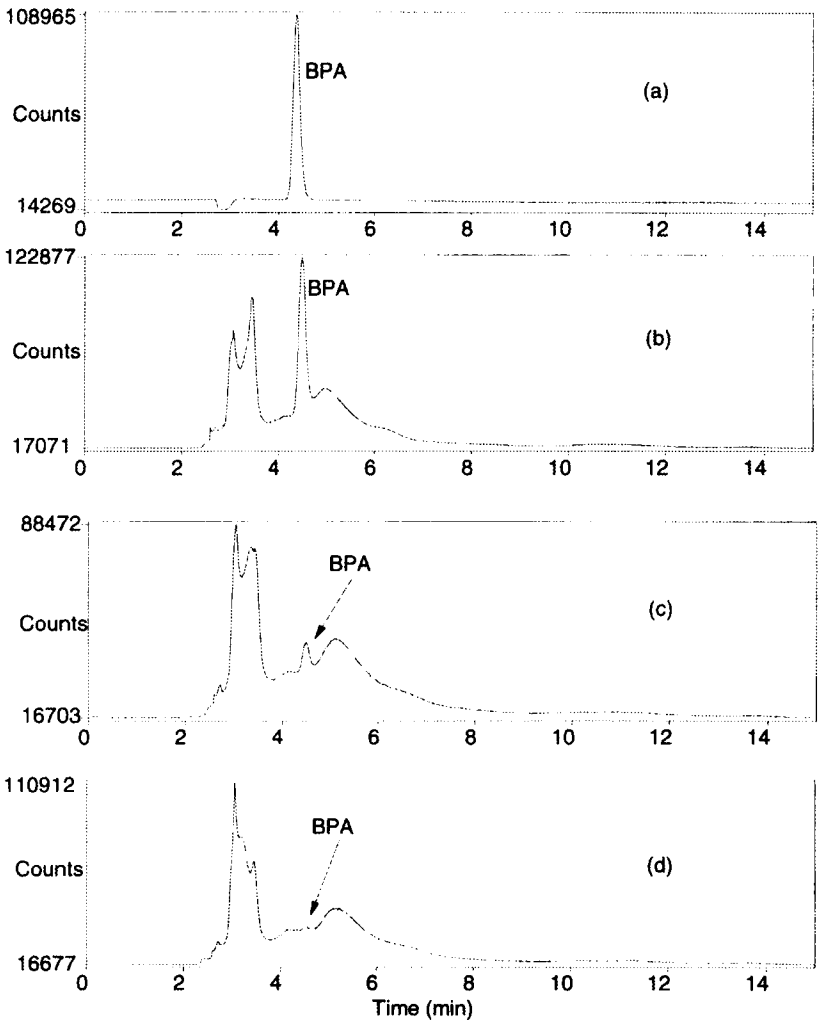

FIGURE 2 HPLC/Fluorescence Chromatograms of a) 99 ng BPA/mL Deionized water Standard. b) 99 ng BPA/mL Patrick's Bayou (PB) water. c) 13 ng BPA/mL PB water. d) 3 ng BPA/mL PB water

The above method development experiments led to the development of a COC-GC-MS method to quantitate and confirm BPA in surface water down to 1 μg/L. This method was selected based on the following strengths. The use of liquid/liquid extraction and room temperature concentration in conjunction with COC injection to minimize thermal degradation of BPA analogs if present in a given matrix. The use of capillary GC would provide exceptional separation capabilities. The use of EI/MS would provide a high level of specificity employing single ion monitoring to obtain the M^+ (228)/$[M\text{-}CH_3]^+$ (213) ion ratio as a BPA confirmation criteria and provide the necessary sensitivity.

The full scan electron impact mass spectrum for BPA is shown in Figure 3. The spectrum shows a peak at m/z 228 corresponding to the M^+ (molecular ion) of BPA. In addition, this spectrum shows a base peak at m/z 213 corresponding to the ($[M\text{-}CH_3]^+$) ion. The m/z 213 ion was chosen for quantitation of BPA to achieve the greatest sensitivity. The confirmation of BPA was based on the M^+ (228)/$[M\text{-}CH_3]^+$ (213) ratio which would be constant if the response for these ions was due to BPA alone. The corresponding M^+ (221) and $[M\text{-}CH_3]^+$ (236) ions were also monitored for the D_8-BPA internal standard. COC-GC-MS ion chromatograms obtained from a river water control sample and a river water sample fortified with 1 ng BPA/mL water and 10 ng D_8-BPA/mL water are shown in Figure 4a and 4b.

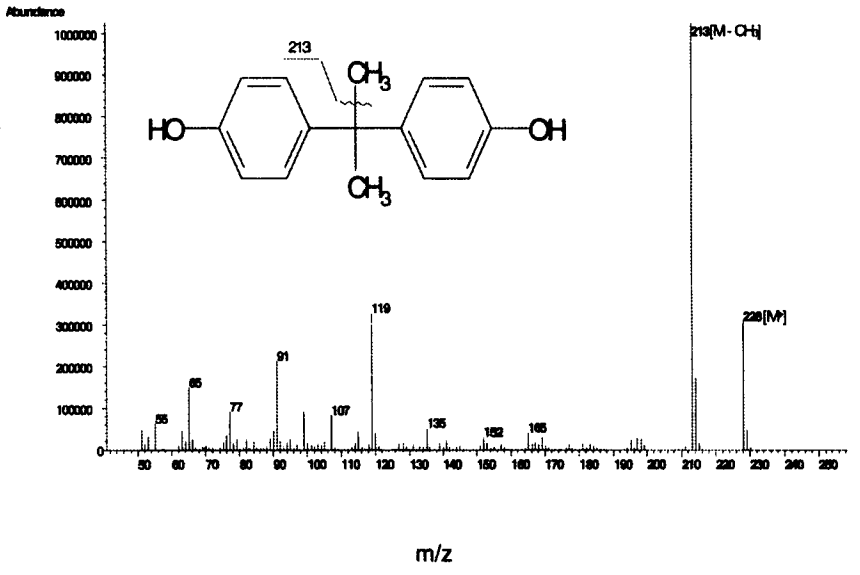

FIGURE 3 GC/EI/MS full scan mass spectrum of a matrix standard containing BPA

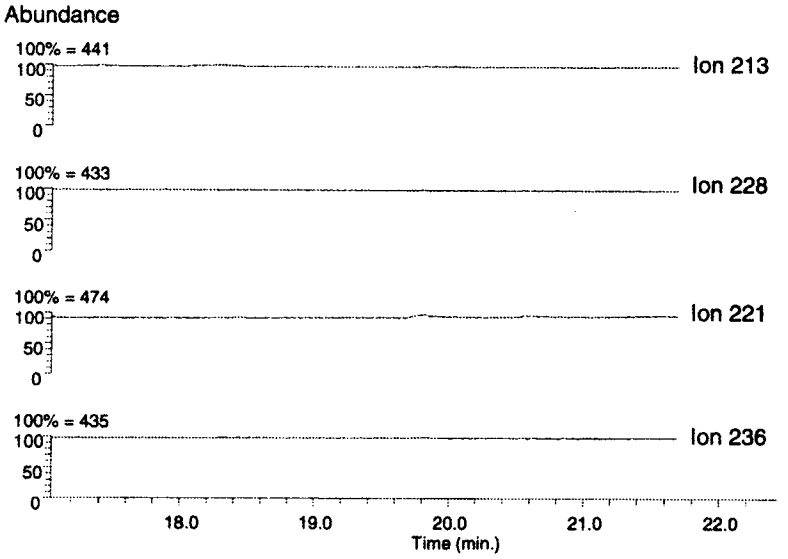

FIGURE 4a COC-GC-MS selected ion chromatograms from a control river water sample

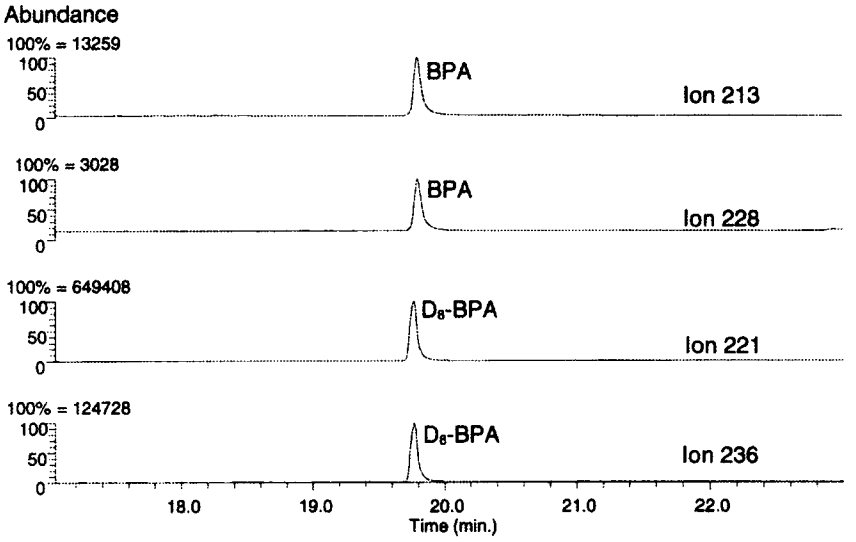

FIGURE 4b COC-GC-MS selected ion chromatograms from a matrix standard of BPA (concentration of BPA = 1 ng/mL; concentration of D_6-BPA = 10 ng/mL)

As stated earlier, the limit of quantitation was set at 1 μg/L and was selected based on the estimated chronic toxicity level of 100 μg BPA/L water and a 100 fold safety factor. Using this method, a 1 μg/L standard produces response at approximately 15× noise for the quantitation ion at m/z 213. The confirmation ion at m/z 228 response at this concentration represents approximately 5× noise making it possible to confirm BPA at 1 μg/L. This method was used to simultaneously quantitate and confirm BPA in river water samples obtained from the five sites (identified in the introduction) and river water samples from each site fortified at approximately 10 μg BPA/L water (field fortified samples). The method was validated from 1 μg/L to 20 μg/L using control river water from the five study sites and deionized water. Matrix (deionized water) standards with levels of BPA within this range (1-20 μg/L) were plotted versus the peak area ratios of ions m/z 213 to m/z 221. These data were then fit to a power curve resulting in a equation of the form Corrected Peak Area Ratio = m * Concentration^b. Typical correlation coefficients (r^2) from these equations were 0.9981 to 0.9999.

Method Validation

Method validation was based on relative recoveries of BPA from deionized water and control river water fortified at concentrations of 1 to 20 μg/L. These data are summarized and presented in Table I and organized as intraday (within) and interday (between) recoveries. These data include the field fortified sample results from the river water study.

Also included in Table I are the average confirmation ion ratios, expressed as a percentage of ion m/z 228 to m/z 213, for the matrix standards and fortified samples of each analysis, in addition to the average for all the matrix standards and fortified samples. The daily analysis confirmation ratios for all the validation samples were within 2% variation of the average confirmation ratio from the standards. This is well within the 25% variation from standards criteria set for the river water study.

Method Application

This method was used to simultaneously quantitate and confirm BPA in river water samples from the five BPA manufacturing sites identified previously. No BPA was detected in the river water samples (n = 5 per site) obtained from the five sites with a detection/confirmation limit of 1 μg BPA/L water. The average recovery for the field fortified samples (10 μg/L) from four of the sites was 103 ± 4%. The initial field fortified samples from Patrick's Bayou (Texas) showed no

TABLE I Relative Recoveries of BPA from Deionized water and Control river water fortified with 1 to 20 ng BPA/mL water.

NominalConcentration	Analysis#1	Analysis#2	Analysis#3	Analysis#4	Analysis#5	Analysis#6	Analysis#7	Analysis#8	Inter-DayAvg.	Inter-DayStd. Dev.
1 μg/L	95 ± 6% n = 3		97%	106%	114%	94%	110%	104%	9%	
2 μg/L	102 ± 4% n = 3		102%	102%	103%	101%	102%	102%	1%	
5 μg/L	100 ± 6% n = 9		98%	101%	103%	100%	102%	101%	2%	
10 μg/L	104 ± 8% n = 9	96 ± 2% n = 6	97 ± 2% n = 6	101 ± 4% n = 13	102%	101%	99%	102%	101%	2%
20 μg/L	107 ± 6% n = 3		97%	97%	96%	95%	100%	97%	2%	
Confirmation Ratio										
Standards	18 ± 2%	21 ± 1%	22 ± 2%	22 ± 2%	19 ± 1%	19 ± 1%	19 ± 1%	23 ± 2%	20 ± 2%	
Samples	17 ± 1%	21 ± <1%	21 ± 1%	20 ± <1%	19 ± <1%	19 ± <1%	19 ± 1%	23 ± 2%	20 ± 2%	

Confirmation Ratio = (ion 228 response/ion 213 response) × 100

BPA present, which made the BPA determination from this site suspect. The known biodegradation of BPA in acclimated systems,[2] the observed instability of BPA in the Patrick's Bayou water (see stability paragraph below), and a documented delay in the shipment of one day for the samples may have accounted for the loss BPA in these field fortified samples. This site was resampled and a more extensive field fortified sample set was included to investigate the loss of BPA and ensure the integrity of the original data. In addition to new field fortified samples (10 μg/L), to duplicate previous data, the additional field fortified samples included samples which were fortified (10 μg/L) and extracted immediately on-site, fortified samples (10 μg/L) treated with HCL to attenuate biological activity, samples fortified at 10× (100 μg/L) the original level, samples fortified with analyte (10 μg/L) and internal standard (100 μg/L) and extracted immediately on-site, and deionized water fortified (10 μg/L) on-site. All fortified samples were prepared in triplicate. The results of the resampling showed no detectable BPA in unfortified Patrick's Bayou water. The data from the expanded field fortified samples indicates that degradation of BPA was the probable cause of the loss of BPA in the original field fortified samples. This conclusion, although not definitive, is based on the comparison of each group of replicate field fortified samples. The repeat fortified samples (10 μg/L) showed a recovery of 92 ± 4% while the fortified samples extracted on-site showed a recovery of 100 ± <1%. Also, the control water fortified samples (10 μg/L) showed a recovery of 108 ± 4%. The 10× (100 μg/L) fortified samples showed a recovery of 99 ± 6% and the HCL attenuated fortified samples (10 μg/L) showed a recovery of 114 ± 1%. The loss of BPA in the field fortified samples (10 μg/L) from the resampling was not complete, as was the case in the initial sampling. However, it is important to note that the composition of the Patrick's Bayou matrix may have been different at the time of the resampling. Although the resampling was conducted at low flow conditions to mimic the original samples, these conditions were achieved following an extended period of heavy rains which may have reduced the biological activity in Patrick's Bayou. In addition, unlike the original samples, the resampling samples experienced no delay in shipment (received overnight).

Stability

The stability of BPA in three river water matrices (Ohio River, OH; Alabama River, AL; Patrick's Bayou, TX) at 5°C was examined on day 0, day 4 and day 17 at a BPA level of 10 μg/L. The results of these experiments are shown in Table II. BPA was shown to be stable in all three matrices after 4 days of storage at 5°C. However, after 17 days of storage (5°C), only 74% of the BPA fortified

TABLE II Stability of BPA in refrigerated (5°C) river water after 0, 4, and 17 days storage and of BPA in Toluene extracts of water stored at room temperature for 17 days.

SampleMatrix	Day 0	Day 4	Day 17
Ohio River	110 ± 4%	98 ± 1%	98 ± 1%
Alabama River	107 ± 3%	97 ± 1%	97 ± 2%
Patrick's Bayou	96 ± 7%	93 ± 1%	74 ± 2%
Toluene Extracts	N/A	N/A	98 ± 2%
Confirmation Ratio			
Standards	18 ± 2%	21 ± 1%	22 ± 2%
Samples	17 ± 1%	21 ± <1%	21 ± 1%

Confirmation Ratio = (ion 228 response/ion 213 response) × 100

into the Patrick's Bayou (Texas) water was recovered. The other two matrices (Ohio River, Alabama River) showed stability after 17 days storage with 98 ± 1% and 97 ± 2% recoveries respectively. In addition, BPA was shown to be stable in toluene extracts at room temperature for 17 days with relative recovery of 98 ± 2% (data also shown in Table II). The average confirmation ion ratios for the storage stability samples are also presented in Table II. These data demonstrate the importance of field fortified samples at each sampling site and at each sampling time point. Field fortified samples provided valuable information to ensure the integrity of the sample collection, shipment, and preparation and analysis. This practice provides a high degree of confidence in the data generated and can help troubleshoot inconsistencies in each phase of a study.

Filter Recovery

The results of the filter recovery experiments, conducted in river water from all five sites in the study, showed an average of 95 ± 1% of ^{14}C-BPA remaining in the five water matrices tested after filtration through Whatman 13mm, 0.7 um GF/F filters. This data demonstrates that the Whatman filters used would not remove BPA dissolved in aqueous matrices and would be appropriate to remove particulates from water samples.

CONCLUSIONS

A sensitive and selective COC-GC-MS method to determine BPA in surface water streams has been developed. This method employs D_8-BPA as an internal standard to improve accuracy and precision. This method also uses liquid/liquid extraction, room temperature concentration and COC injection to reduce the

chance of false positives for BPA resulting from the thermal degradation of BPA analogs which may be present. Also, this method uses mass spectrometry to obtain simultaneous quantitation and confirmation of BPA at a detection limit of 1 μg BPA/L water. The method has been validated from 1 to 20 μg BPA/L water and has been used successfully to determine the level of BPA in five different surface water streams at a single point in time (Oct./Nov. 1996).

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References

[1] USEPA. 1994. Preliminary Exposure Profile for Bisphenol A. U.S. Environmental Protection Agency, OPPT, Washington, DC.
[2] P.B. Dorn, C.S. Chou and J.J. Getempo, *Chemosphere*, **16**, 1501-1507 (1987).
[3] C.A. Staples, D.A. Markham, and D.A. McNett, Analysis of Surface Water Receiving Streams for Bisphenol A (1997), Unpublished report for SPI.
[4] H.C. Alexander, D.C. Dill, L.W. Smith, P.D. Guiney, and P.B. Dorn, *Environ. Toxicol. Chem.*, **7**, 19-26 (1988).
[5] AG Bayer, Studies on the Ecological Behavior of Bisphenol-A. Study No. 600 A/96/0057/00 LEV, ZF-DZA Test Institute, Germany, (1996).
[6] J. Simal Gandara, S. Paz Aubin, P. Paserio Losada, J. Simal Lozano, *J. Chromatogr. Sci.*, **31**, 450-454 (1993).
[7] N. Olea et. al., *Env. Health Perspectives*, **104**, 298-305 (1996).
[8] K. Blau and J. Hlket, *Handbook of Derivatives for Chromatography* (John Wiley & Sons, New York, 1993) 2nd ed., Chap. 3, pp 44-45.
[9] D.R. Knapp, *Handbook of Analytical Derivatization Reactions* (John Wiley & Sons, New York, 1993) Chap. 1, pp 48-63.
[10] Unpublished internal Dow Chemical Company report.
[11] M.P. Barbalas and W.A. Garland, *J. Pharm. Sci.*, **80**, 922-927 (1991).