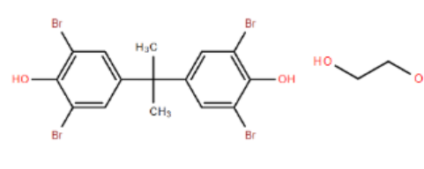
APWC 2017
POSTER D-09

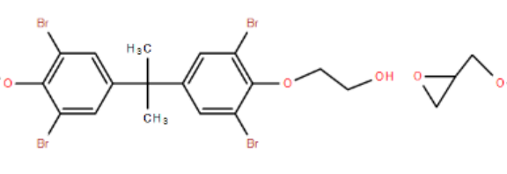
Determination of tetrabromobisphenol A/S and their main derivatives in water samples by HPLC-ICP-MS/MS

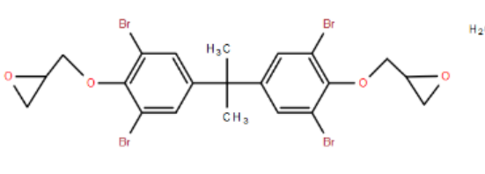
Lihong Liu[1], Zhaojun Yun[2], Aifeng Liu[1], Qinghua Zhang[1, *], Jianbo Shi[1], Bin He[1] and Guibin Jiang[1]
1. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 100085, Beijing
2. Agilent Technologies (China) Co., Ltd., Beijing 100102, China
Corresponding author email: qhzhang@rcees.ac.cn

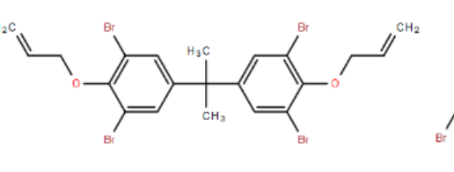
Introduction

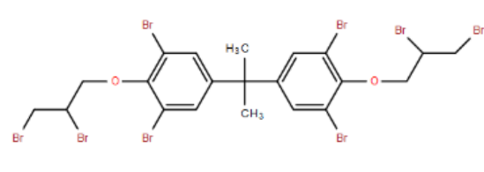
Brominated flame retardants (BFRs) have been widely used in various consumer and many fields of our lives. Tetrabromobisphenol A (TBBPA) is the most widely used BFRs with production volume representing about 60% of the total BFRs market. Recently, TBBPA as well as its alternative Tetrabromobisphenol-S (TBBPS) and their derivatives have raised public concerns due to their persistence, bioaccumulative ability and potential adverse effects on human health[1]. To study the environmental behavior and evaluate the potential health impact of these BFRs, it was important to develop sensitive analytical methods for the determination of TBBPA/S and their derivatives in real samples.

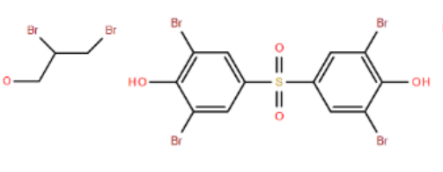

TBBPA

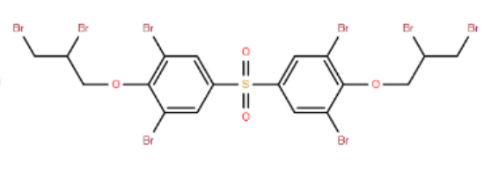

TBBPA-BHEE


TBBPA-BGE


TBBPA-BAE


TBBPA-BDBPE


TBBPS


TBBPS-BDBPE

Nowadays, the analytical methods for TBBPA were mainly based on gas chromatography -mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS)[2]. However, there are still lack of sensitive methods for determination of TBBPA derivatives, especially for TBBPA-bis(allylether) (TBBPA-BAE) and TBBPA-bis(2,3-dibromopropyl ether) (TBBPA-BDBPE).

In this work, the inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) was used as a sensitive detector for the quantification of these BFRs and a novel analytical method was established by coupling HPLC with ICP-MS/MS for the determination of TBBPA/S and their derivatives [3].

Experiment

The experiments were carried out by using a high performance liquid chromatography (HPLC, Agilent 1200 HPLC Pump, Agilent Technologies Inc., Germany) coupled with inductively coupled plasma tandem mass spectrometry (ICP-MS/MS, Agilent 8800, Agilent Technologies Inc., Tokyo, Japan). The ICP-MS instrument was tuned and optimized for the quantification of Br (m/z 79) at the beginning of the experiment every day. The operating conditions of HPLC-ICP-MS system were summarized in table 1. The water samples were extracted by liquid-liquid extraction after filtration through 0.45 μm membranes prior to the analysis [3].

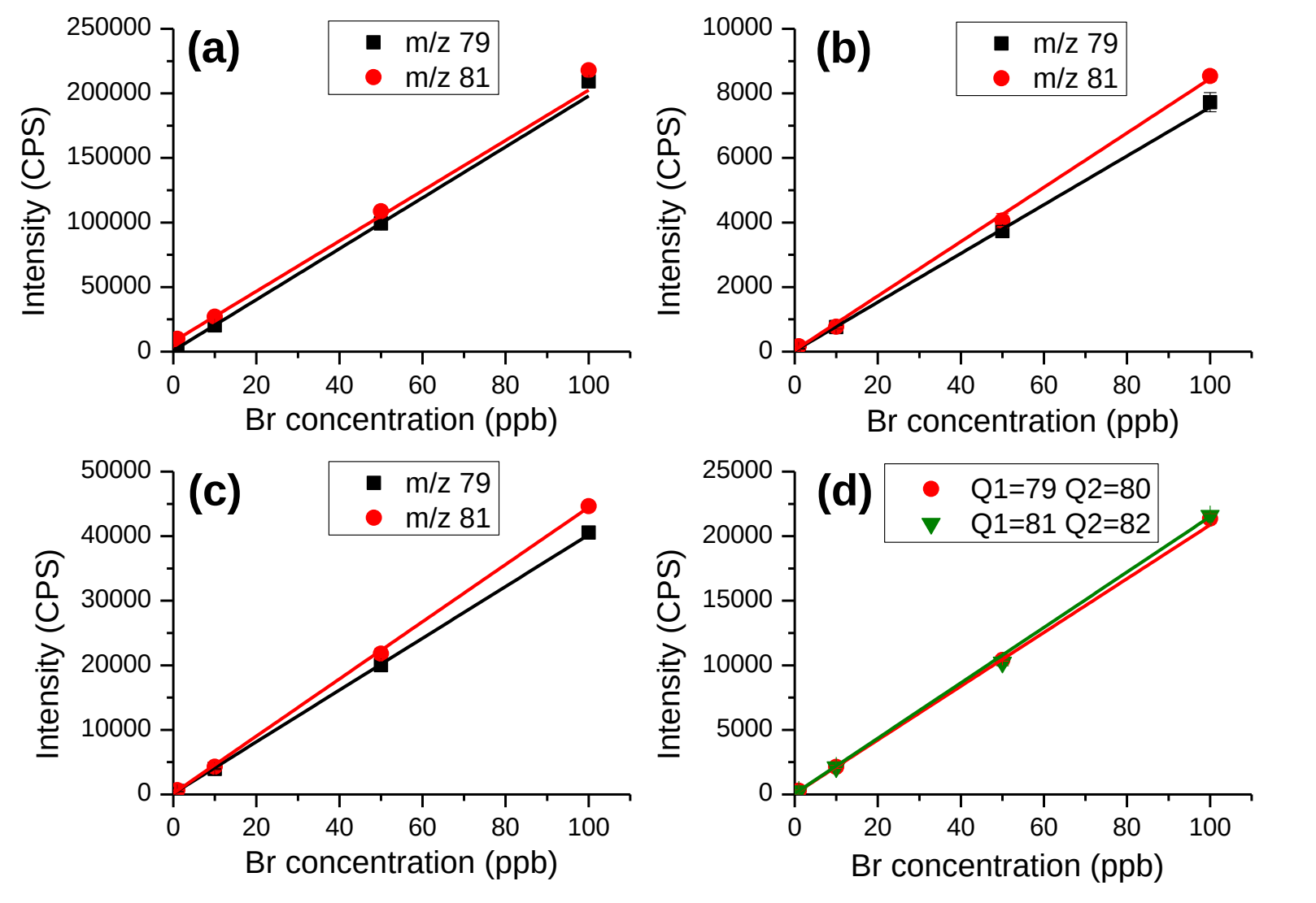


Figure 1 The calibration curves of ^{79}Br and ^{81}Br under different ICP-MS detection mode: (a), no gas mode; (b), CRC mode with He as reaction gas; (c), CRC mode with H_2 as reaction gases; (d), CRC mode with H_2 as reaction gases under "mass-shift mode" measurement.

Table 1 The HPLC-ICP-MS conditions

HPLC	
Column	ZORBAX Eclipse Plus C18 column, 150×4.6 mm, 5 μm
Mobile phase (MB)	A: methanol (0.1% (v/v) acetic acid);B: H_2O (0.1% (v/v) acetic acid) 0~3 min, from 80 to 90% A, from 20% to 10% B; 3~12 min, from 90 to 100% A, from 10% to 0% B; 12~15 min, 100% A, 0% B; 15~16 min, from 100 to 80% A, from 0% to 20% B; 16~20 min, 80% A, 20% B; 20 min, stop
Flow rate of MB	1.0 mL min^{-1}
Injection volume	50 μL
ICP-MS	
RF Power	1600 W
Smpl Depth	8.0 mm
Carrier Gas	0.4 L/min
Makeup Gas	0 L/min
Optional Gas	30% optional gas, containing 20% O_2 in Ar
Reaction gas	H_2, 4.5 mL/min
peristaltic pump	0.3 rps
Temperature of spray chamber	-5 ºC
Monitored isotope (m/z)	Q1, 79 (Br^+) → Q2 79 (Br^+)
Integration time	0.5 s

Table 2 The analytical performance of the developed HPLC-ICP-MS method.

Analytes	Linear Range (μg L^{-1})	Correlation coefficient	**LOD[a] (μg L^{-1})**	**IDL[b] (pg)**	RSD (%) Intra-day[c]	RSD (%) Inter-day[d]
TBBPA	5-200	0.9991	**0.12**	**6**	2.0	6.5
TBBPA-BHEE	5-200	0.9993	**0.14**	**7**	1.5	5.8
TBBPA-BGE	5-200	0.9995	**0.19**	**9.5**	1.8	5.9
TBBPA-BAE	5-200	0.9995	**0.14**	**7**	2.2	6.8
TBBPA-BDBPE	5-200	0.9996	**0.12**	**6**	1.9	7.3
TBBPS	5-200	0.9994	**0.17**	**8.5**	1.7	6.5
TBBPS-BDBPE	5-200	0.9996	**0.13**	**6.5**	1.9	6.7

[a] The LOD was calculated based on the 3S/N.
[b] Absolute detection limits (pg) based on a 50 μL sample injection.
[c] RSDs of intra-day, 100 μg L-1, n = 5.
[d] RSDs of inter-day, 100 μg L-1, n = 1 per day for 5 days.

Results and discussion

To eliminate the spectral interferenceand and obtain higher sensitivities, both the no gas mode and the collision/ reaction cell (CRC) mode of ICP-MS/MS were evaluated and optimized. The use of reaction gases significantly eliminated the interferences and decreased the baseline values of ^{79}Br and ^{81}Br in comparison with the no gas mode and hydrogen (H_2) was selected as the most appropriate reaction gas for the detection of Br (Figure 1). Besides, to maintain a stable plasma and reduce carbon deposits on the torch and the cones caused by the introduction of organic solvent in the mobile phase of HPLC, the optional gas of oxygen (O_2, containing O_2 20% in Ar) was used and the optional gas ration was optimized to be 30%.

Under the optimized conditions, seven BFRs including TBBPA, TBBPA-BHEE, TBBPA-BGE, TBBPA-BAE, TBBPA-BDBPE, TBBPS and TBBPS-BDBPE were baseline separated and sensitivity quantified by determination of bromine (m/z=79) (Figure 2). The relative standard deviations (RSDs) were less than 2.2% for the peak area and 0.2% for the retention time, representing high precision and good repeatability. The instrumental limits of detection (LOD) for the BFRs were in the range of 0.12 - 0.19 μg mL^{-1} (Table 2), which was close or one to three orders of magnitude lower than the reported methods [4]. The proposed method was successfully applied for analysis of river water, tap water and sea water samples (Figure 3) as well as soil samples collected from the industrial area. The spiked recoveries at different spiking concentrations were in the range of 67.7% - 113%, which showed that the HPLC-ICP-MS was a reliable technique for the determination of novel BFRs.

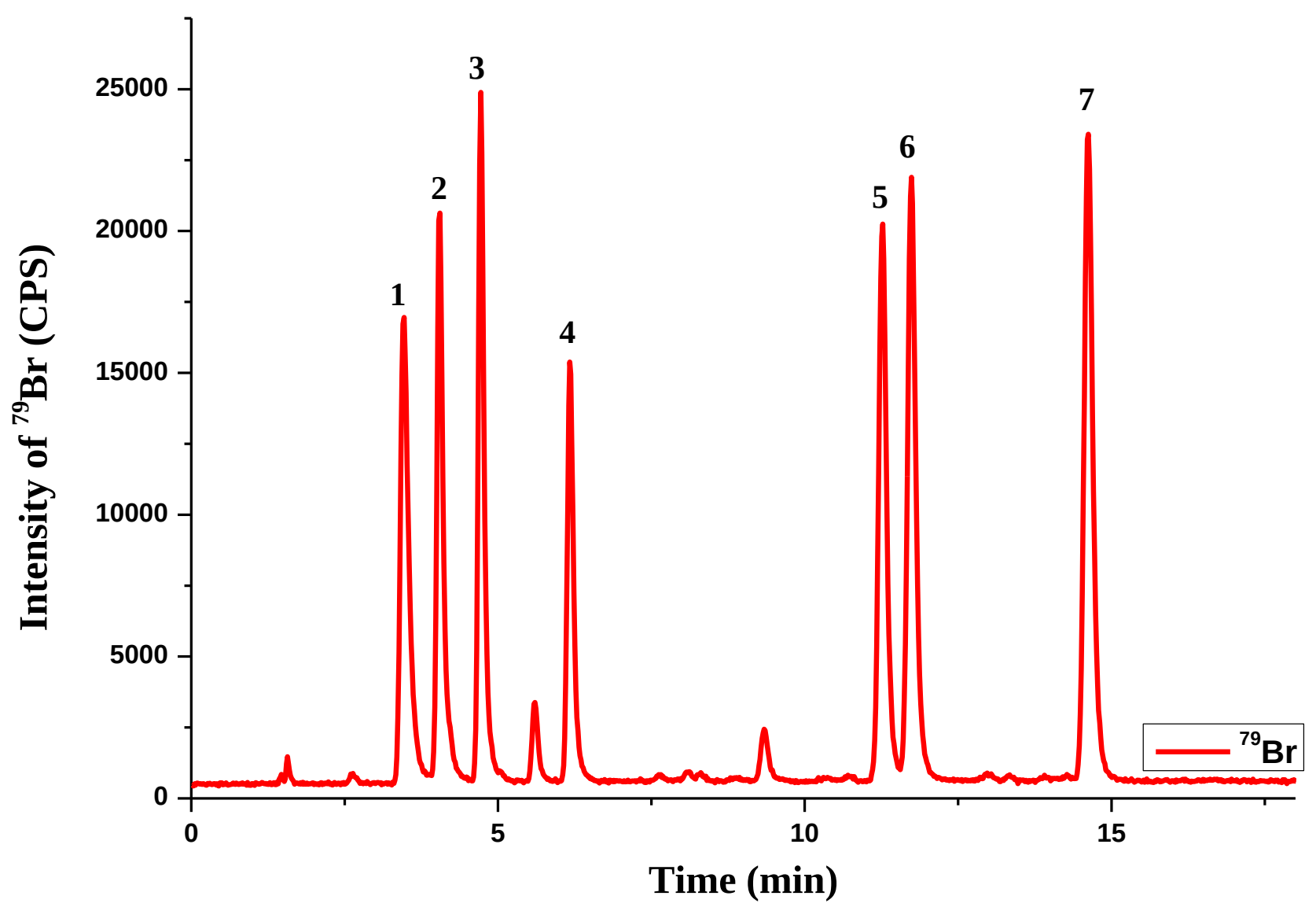


Figure 2. HPLC-ICP-MS chromatography of mixed standard solutions (100 g L^{-1}) under the optimized conditions. (1, TBBPS; 2, TBBPA-BHEE; 3, TBBPA; 4, TBBPA-BGE; 5, TBBPA-BAE; 6, TBBPS-BDBPE; 7, TBBPA-BDBPE.

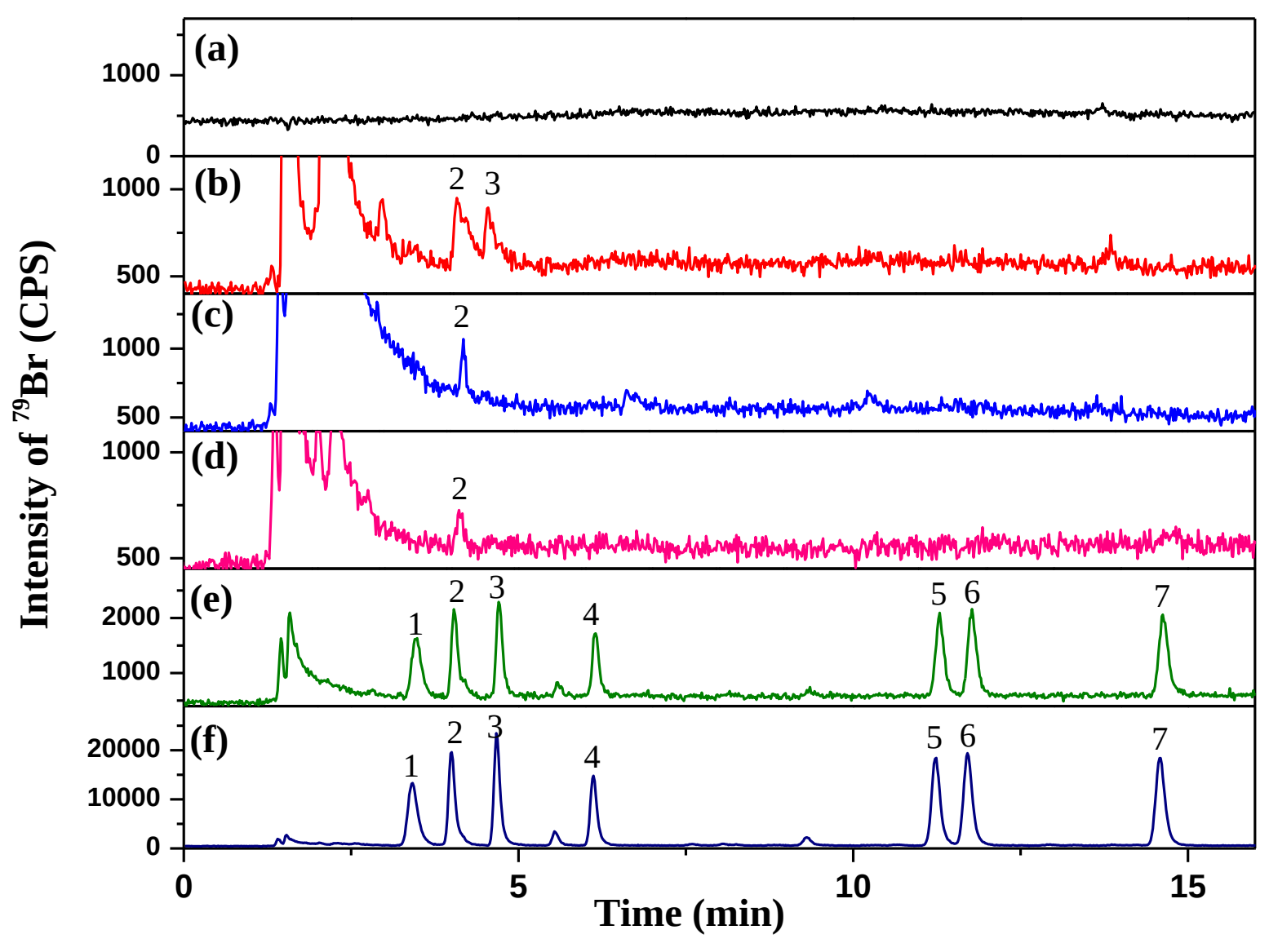


Figure 3. HPLC-ICP-MS chromatography of TBBPA/S and the derivatives in water samples: (a) blank; (b) sea water; (c) river water; (d) tap water; (e) tap water spiked with 0.05 μg L^{-1} of each BFR; (f) tap water spiked with 0.5 μg L^{-1} of each BFR.

Conclusion

In this work, a novel method for the determination of TBBPA/S and their derivatives has been developed based on the HPLC-ICP-MS/MS hyphenated techniques. The method enables fast separation and sensitive quantification of seven TBBPA/S and their derivatives in water samples. The proposed method provided an alternative and sensitive tool for the analysis of TBBPA/S and derivatives in water samples and may be applied to more complex samples such as environmental and biological samples in the future. Moreover, this study also provide significant new insight into the determination of novel bromine containing organic compounds by ICP-MS.

References

[1]. R.J. Letcher; S. Chu; Environ. Sci. Technol. 2010, 44 8615-8621
[2]. Qu, G.; Liu, A.; Jiang, G.; et al.; Trends in Anal. Chem. 2016, 83, 14-24
[3]. Liu, L.; Liu,A.; Yun, Z.; et al.; J. Chromatogr. A 2017, 1497, 81-86
[4]. Tian, Y.; Liu, A.; Jiang, G.; et al.; RSC Advanves. 2015, 5, 14476-14479