

TETRACHLORBENZO-P-DIOXINS DETERMINATION IN SURFACE AND SEWAGE WATER USING GC, GC-LRMS AND GC-HRMS

E.S. Brodsky, V.G. Jilnikov, N.A. Kijuev, A.K. Prokofjev, N.V. Murenetz, B.V. Bocharov

Institute of Animal Evolutionary Morphology and Ecology USSR Academy Sciences, Moscow

Introduction

Determination of polychlorinated dibenzo-p-dioxins (PCDD) and related compounds in the environment can be performed by a combination of hardly compatible and often excluding conditions: extremely high sensitivity (detection limit 1 pg and lower) and high specificity for reliable separation and identification and correct determination.

Usually capillary GC with electron capture detector (GC-ECD), GC-LRMS and GC-HRMS are used for trace levels of PCDD and related compounds determination in environment; GCMS/MS is used less often.

This report provides a brief description of a study on the evaluation of reliability of data from capillary GC-ECD, GC-LRMS in full scan and selected ion detection (CID) modes and GC-HRMS on tetrachlorodibenzo-p-dioxins (TCDD) determination in surface and sewage water. These methods were used for analysis of industrial incinerator and cellulose mill sewage water, lake water of Baykal and drinking water.

Experimental

1 L water sample fortified with 10 ng $^{13}\text{C}_6$ -1,2,3,4-TCDD and 1 μg bis(p-bromo-phenyl)ether (BBPE) followed by extraction with methylene chloride; treatment with concentrated sulfuric acid and sodium hydroxide and concentrating on a Kuderna-Danish apparatus.

A HP 6890A with ECD and fused silica capillary column SP2331, 40 m x 0.25 mm for GC analysis; a Finnigan MAT ITD 700 ion trap coupled with gas chromatograph HP 5890A equipped with fused silica column SE 30 25 m x 0.25 mm for GC-LRMS; a Finnigan MAT H-SQ 30 high resolution mass spectrometer coupled with a Varian model 3400 gas chromatograph with fused silica capillary column DB-5 (25 m x 0.25 mm) or SP-2331 (60 m x 0.25 mm). Temperature programs were: for GC- from 60 °C (hold 2 min) to 180 °C with rate 20 °C/min, then to 250 °C with rate 3 °C/min and holding at this temperature for 20 min; for GC-LRMS - from 60 °C (hold 1 min) to 240 °C with rate 10 °C/min and hold at that temperature; for GC-HRMS - rapid increasing from 210 °C to 250 °C and holding at that temperature for DB-5 and from 180 °C to 250 °C and holding for SP 2331.

Selected ions monitored were m/z 319.897, 321.894 for TCDD and 327.914 for $^{13}\text{C}_6$ -1,2,3,4-TCDD.

Results and Discussion

Evaluated TCDD extraction efficiency was 92.6%, detection limit for standard solutions 0.1 pg. ECD chromatographs of five industrial incinerator sewage water samples have a number of peaks in the TCDD retention time area, some of them are very close or identical to the TCDD isomer standards. But GC-HRMS did not confirm TCDD in some samples. In others only 2,3,7,8-TCDD was found (see table). In sample 2 some small peaks in the TCDD retention time area showed interference with background "hump".

TCDD content in incinerator sewage water samples

No.	Concentration ng/L (GC)	Ratio of m/z 319.897 and 321.894	Concentration ng/L (GC-HRMS)	
1	-	-	-	-
2	67	0.757	71.1	5.3
3	-	-	-	-
4	-	0.722	23.0	4.1
5	44	0.753	47.4	3.8

TCDDs were not found in cellulose mill sewage water, lake water and drinking water samples.

The GC detection limit for TCDD in complex matrices rises dramatically. It is about 5-10 pg.

GC-LRMS detection limit is about 0.1 ng when full scan mode is used, and this sensitivity is not enough for trace level TCDD determination. In CID mode the sensitivity is two orders of the magnitude better (detection limit is about 1 pg) and specificity is much better, but if the mixture contains interfering compounds (polychlorinated phenoxy-phenols, diphenylethers etc.) TCDD identification can be ambiguous.

GC-HRMS provides high sensitivity (detection limit is 1 pg and lower) and high specificity, also an effective quality control is possible.