High Sensitivity Analysis of Formaldehyde using NCI-GC/MS

In June 1998, the Japanese Environment Agency created a list of items to be monitored for water environmental preservation, where 300 substances are listed. Procedure manuals for monitoring these substances issued by the Water Quality Bureau of the Environment Agency issued in December 1999 includes the method for analyzing formaldehyde, one of the substance to be monitored. According to this method, formaldehyde is derivatized with PFBOA (pentafluorobenzylhydroxylamine) (see Scheme 1), and the produced PFBOA formaldehyde is analyzed by GC/MS. Quantitation should be conducted by SIM measurement with the EI (Electron Ionization) method.

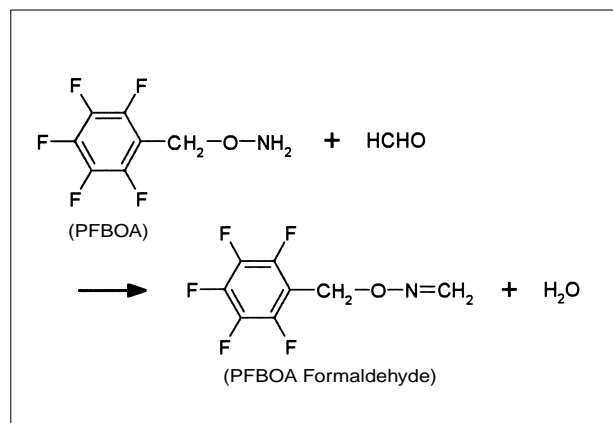In the example introduced here, PFBOA formaldehyde was measured using the prescribed EI method, and also the NCI (Negative Ion Chemical Ionization) method.

The NCI method detects negative ions generated by ion-molecular reaction or by electron capture reaction. This method achieves high-sensitivity analysis of compounds with high electron affinity, as well as halogenated compounds like PFBOA formaldehyde.

SIM measurement with the NCI method (Fig. 7) achieved sensitivity 100 times higher than that of the EI method (Fig. 3) for PFBOA formaldehyde. As proved here, formaldehyde can be detected with higher sensitivity by using the NCI method.

Table 1 Analytical conditions

-GC-	
Column	: DB-1 (30 m×0.32mm I.D. df = 0.25μm)
Column Temp.	: 40˚C(2min)-10˚C/min-150˚C
Carrier Gas	: He, 150kPa at 40˚C
Injector Temp.	: 250˚C
Injection Method	: Splitless(Sampling Time 1min)
Injection Volume	: 2μL
-GCMS-	
Interface Temp.	: 250˚C
Ionization Method	: EI
	NCI(i - C_4H_{10}, 100kPa)
Scan Range	: m/z 40-300
Scan Interval	: 0.5sec
SIM	: 0.2sec EI m/z 181, 195
	NCI m/z 181, 178, 175, 197

Scheme 1 PFBOA Derivatization of Formaldehyde

Sample Name:PFBOA-EI-scan-10ppm
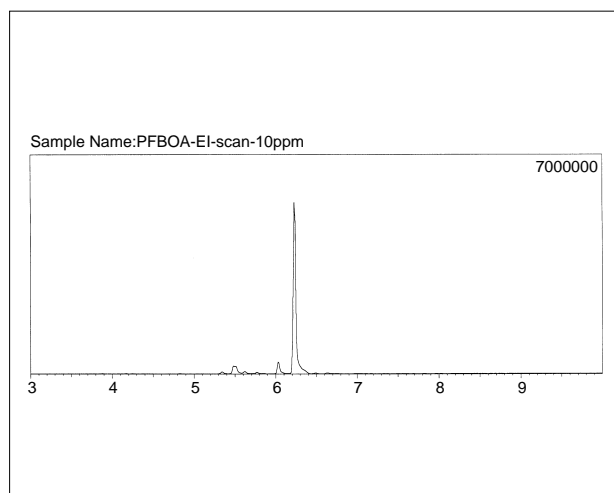
Fig.1 TIC of PFBOA Formaldehyde

Scan No. : 389   Background : 394
No. of Peaks : 74 Retention Time : 6.233
Base Peak : 181.00 (2832710)

Fig.2 Mass Spectrum of PFBOA formaldehyde : EI

Sample Name : PFBOA-EI-sim-1ppb

TIC 7000

6.255
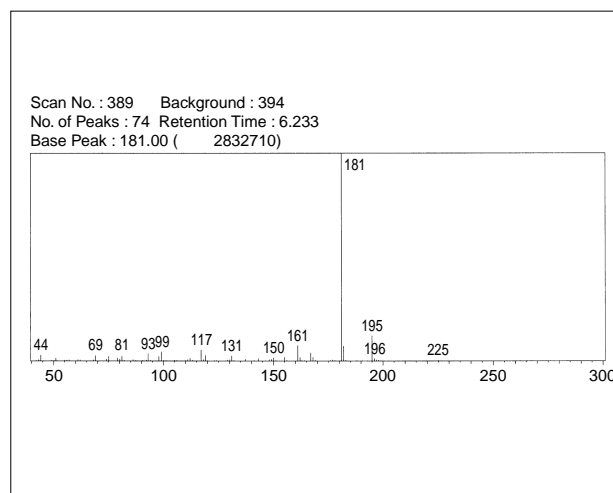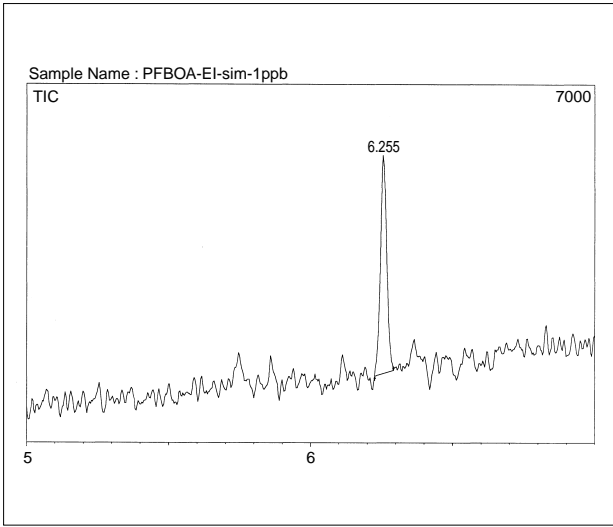
Fig.3 SIM Chromatogram of PFBOA formaldehyde(1μg/L) : EI

ID#1 Mass No. : 181.00 Substance Name : PFBOA-formal dehyde
Area = 1025.88 × Concentration Contribution Rate =0.999278
Area

	Concentration (ppb)	Area
1	100.000	101379
2	50.000	53492
3	10.000	11325
4	5.000	5143
5	1.000	1270
6	0.500	594

Fig.4 Calibration Curve of PFBOA formaldehyde : EI

Sample Name : PFBOA-NCI-scan-20ppb

TIC 11499000
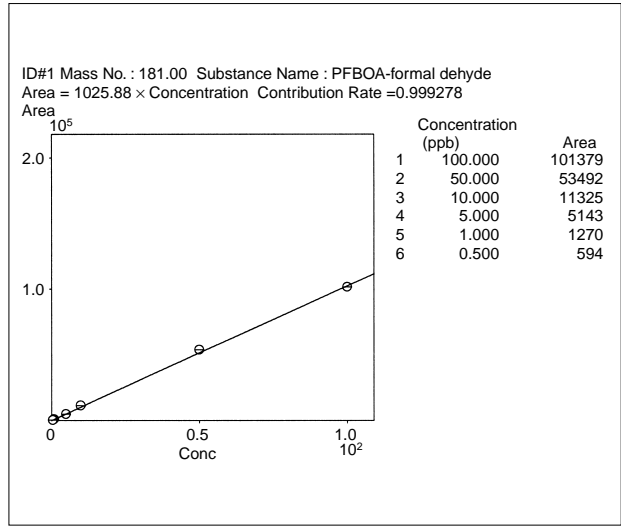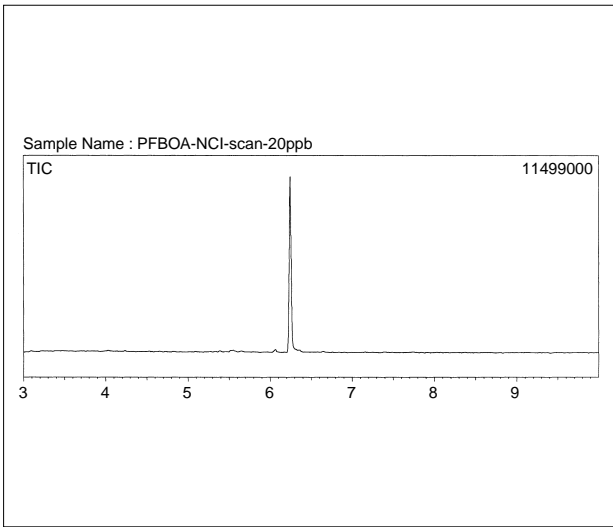
Fig.5 TIC Chromatogram of PFBOA formaldehyde : NCI

Scan No. : 391   Background : 395
No. of Peaks : 30 Retention Time : 6.250
Base Peak:181.00 (4191293)

181

167 197 205 225

Fig.6 Mass Spectrum of PFBOA formaldehyde : NCI

Sample Name : PFBOA-NCI-sim-10ppt

TIC 120000

6.248
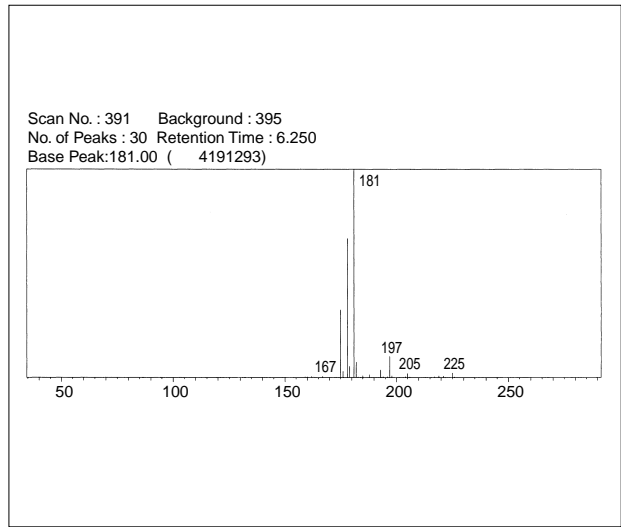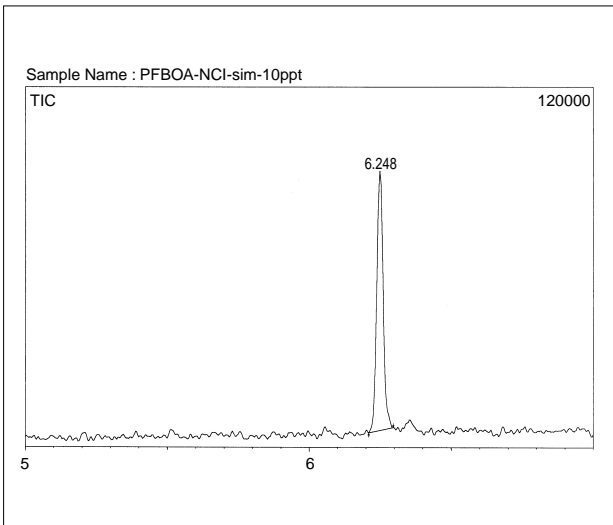
Fig.7 SIM Chromatogram of PFBOA formaldehyde(10ng/L) : NCI

ID#1 Mass No. : 181.00 Substance Name : PFBOA-formal dehyde
Area = 1025.88 ¥ Concentration Contribution Rate =0.999278
Area

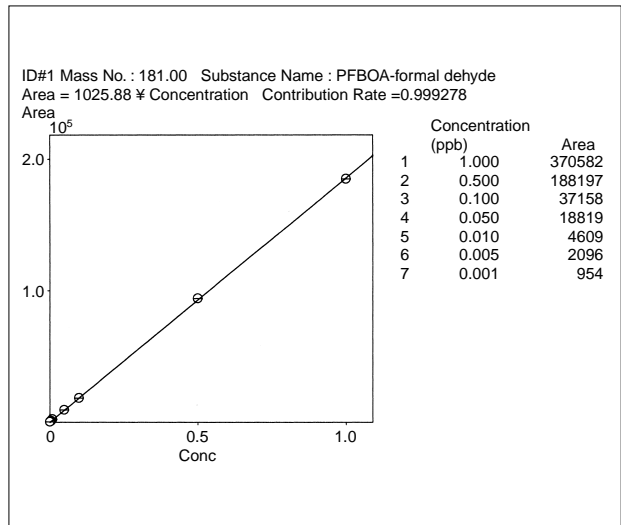|	Concentration (ppb)	Area
1	1.000	370582
2	0.500	188197
3	0.100	37158
4	0.050	18819
5	0.010	4609
6	0.005	2096
7	0.001	954

Fig.8 Calibration Curve of PFBOA formaldehyde : NCI