ANALYSIS OF ALDEHYDES IN FOGWATER BY HPLC WITH POSTCOLUMN REACTION DETECTOR

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Abstract - An analytical procedure that couples HPLC with the postcolumn reaction detector of flow injection method was developed to analyze aldehydes in fogwater samples. The aldehydes were derivatized with 3-methyl-2-benzothiazolinone hydrazone (MBTH) in the reactor and detected at 640 nm. The optimal condition was established and formaldehyde, glyoxal, and glycolaldehyde concentrations were determined. The data obtained by this method were consistent with those obtained by 2,4-dinitrophenylhydrazine (DNPH) method.

Key Words - Postcolumn method, HPLC, Aldehyde, Fogwater, MBTH method

Aldehydes are highly reactive in the atmosphere and hydrophilic aldehydes exist in fogwater. Aldehydes can be determined quantitatively by derivatization with DNPH followed by HPLC analysis[1]. However, the derivatization method is troublesome and their absorbance are affected by the other components in the sample. We have already reported an analytical procedure for aldehydes that couples HPLC with a segmented flow analyzer[2] but its sensitivity is not enough to determine trace amount of aldehydes in environmental samples. In this paper, we will report a novel analytical procedure for aldehydes that couples HPLC with a continuous flow injection analyzer, where aldehydes separated on a reversed-phase column were derivatized with MBTH (3-methyl-2-benzothiazolinone hydrazone)[3], and determine aldehydes in fogwater samples by this method.

EXPERIMENTAL

Analysis The analysis system is shown in Fig. 1. The eluent was a 60%/40% by volume acetonitrile and 0.1% MBTH aq. soln. mixture. Aldehydes in the sample injected were derivatized with MBTH in coil 1 (0.5 x 700 mm) and were separated on an analytical column (Inertsil ODS-2, 5 μ m, 4.6 x 250 mm). The eluent was mixed with 1% Fe(NO₃)₃ aq. soln. in coil 2 (0.5 x 250 mm) and were detected at 640 nm. The concentrations were measured by comparing their peak heights with those of the standard solutions.

Sample Collection Fog samples were collected with a string-type collector at the midslope (700 m above sea level) of Mt. Ohyama in Kanagawa Pref. The samples were stored in a refrigerator from the sampling station to our laboratory and they were stored in a freezer until the analysis.

Fig. 1. Schematic diagram of the apparatus.

RESULTS AND DISCUSSION

The aldehydes were derivatized with MBTH. The derivatization proceeds as shown in Fig. 2; aldehydes react with MBTH to form the corresponding azide; MBTH is oxidized by Fe^{3+} to a reactive cation; and a blue cation forms from a combination of the azide and a reactive cation. In the postcolumn method,

the reaction is proceeded after the separation by a column but MBTH was added to the eluent because hydrophilic aldehyde is difficult to be separated on an ODS column. The first derivatization reaction were achieved prior to the column, the second reaction was proceeded after the column, and then the azides formed from aldehydes and MBTH were separated on the column.

The sensitivity of this method depends on the reaction conditions and the optimal condition was investigated. We compared several oxidizing reagents and $\text{Fe}(\text{NO}_3)_3$ was the most sensitive reagent. The detection sensitivity increased with an increase of MBTH and Fe^{3+} concentrations but the column and the cell were soiled with the high concentrations of MBTH and Fe^{3+} . Then, each reagent concentration was optimized as described in the experimental section. Coils 1 and 2 were thermostated at 60°C because the time taken to react aldehydes with MBTH is about 1 hour at room temperature. The flow rate and the length of coils were also optimized after some experiments. Fig. 3 shows typical chromatogram of aldehydes and the aldehydes can be analyzed with high sensitivity. The calibration curves for many aldehydes gave linear relationships and the correlation coefficients (r^2) were close to 1: 1.000 for formaldehyde, 1.000 for acetaldehyde, 0.998 for glyoxal, 0.999 for glycolaldehyde. Table 1 shows the sensitivities and the detection limits of representative aldehydes. The sensitivity was defined as (absorbance of the peak height)/{(injection volume (L))x(sample concentration (M))} and the detection limit was calculated when the ratio of signal-to-noise was 2. Most of the aldehydes can be easily detected until 1 μM , although the sensitivity decreases with an increase in carbon number.

Aldehydes in the fogwater samples were analyzed by this method. Hydrophilic aldehydes such as formaldehyde, glyoxal, and glycolaldehyde were determined to be in the range of 1 μM to 100 μM . The analytical values were reproducible and the data obtained by this method agreed well with the data obtained by DNPH pre-column method. This method may come in useful to analyze trace amount of aldehydes in environmental samples.

Fig. 3. Typical chromatogram of aldehydes.

Fig. 2. Reaction scheme of aldehyde derivatization.

Table 1. Sensitivity and detection limit of aldehydes.

aldehydes	sensitivity ($\times 10^8$)	detection limit (μM)
HCHO	1.08	0.09
CH_3CHO	0.23	0.36
$\text{C}_2\text{H}_5\text{CHO}$	0.15	0.68
$\text{C}_3\text{H}_7\text{CHO}$	0.10	1.10
CHOCHO	0.06	1.35
CH_3COCHO	0.01	6.89
HOCH_2CHO	0.67	0.16

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