Application News

No. G327A

Analysis of Gas-Phase Formaldehyde by GC-FID Method Utilizing DNPH Derivatization

Formaldehyde has the simplest structure among the aldehydes, but is known to be a harmful air pollutant. Accordingly, various pretreatment processes for trace analysis of the compound have been proposed and established in the past (Application News No. G292, L476).

Flame Ionization Detector (FID) is among the most general detectors used in Gas Chromatography (GC). While FID does not have sensitivity for formaldehyde, it does for DNPH (2,4-dinitrophenylhydrazine)-derivatized formaldehyde. This article examined the quantitation of formaldehyde in gas- phase by GC-FID utilizing DNPH derivatization.

Y. Nagao

■ Analysis of Standards

Table 1 shows the instrument configuration and analytical conditions used in this experiment. Standard solutions were prepared by serially diluting the 100 ng/μL standard solution (2 Aldehydes-DNPH Mixed Standard Solution [P/N: 012-17391; Fujifilm Wako Pure Chemical Corp.]) to 1, 5, 10 and 50 ng/μL in Acetonitrile. Fig. 1 shows the chromatogram of the standard solution prepared. The peak for DNPH-derivatized acetaldehyde was split into two as it contained *syn* and *anti* isomers.

Table 1 Instrument Configuration and Analytical Conditions

|	
Model	: Nexis™ GC-2030AF/AOC-20i Plus
Injection mode	: Split (1:30)
Injection volume	: 1.0 μL
Injection temp.	: 280 °C
Carrier gas	: He
Carrier gas control	: Constant linear velocity (35 cm/s)
Purge gas	: 3.0 mL/min
Column	: SH-1 (30 m × 0.32 mm I.D., 1.00 μm) [*1]
Column temp.	: 240 °C (8 min) - 20 °C /min - 260 °C (2 min)
Detector	: Hydrogen gas flame ionization detector (FID)
Detector temp.	: 280 °C
Detector gas	: H_2 32.0 mL/min, Air 200 mL/min
Makeup gas	: He 24 mL/min

*1 P/N: 221-75725-30
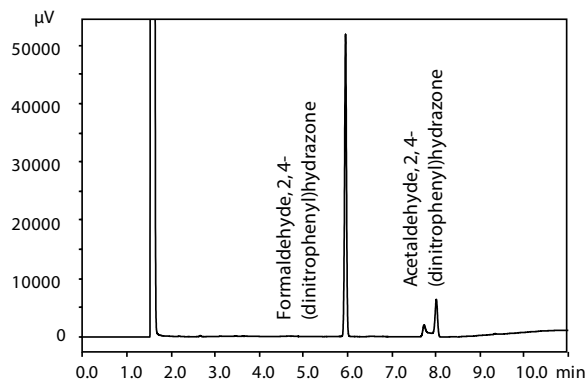
Fig. 1 Chromatogram of 2 Aldehyde-DNPH Mixed Standard Solution (Each at 100 ng/μL)

A calibration curve was prepared by conducting 5 consecutive analyses of each of the standard solutions with concentrations of 1, 5, 10, 50, and 100 ng/μL (Fig. 2). Good linearity was obtained with R^2 of 0.9999 and satisfactory repeatability was confirmed for all concentrations (Table 2). With the S/N of DNPH-formaldehyde at 1 ng/μL measured to be 25.4, the limit of detection (S/N=2) was calculated to be approximately 0.1 ng/μL.
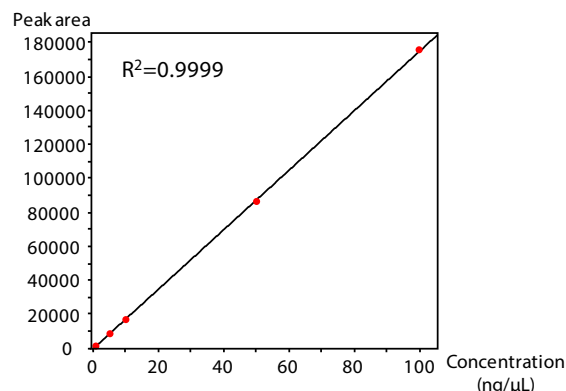

Fig. 2 Calibration Curve of DNPH-Formaldehyde

Table 2 Peak Area Repeatability for DNPH-Formaldehyde (n=5)

Concentration (ng/μL)	1	5	10	50	100
Peak area RSD (%)	2.02	0.48	0.80	0.20	0.12

■ Flow of Gas-Phase Formaldehyde Analysis

Fig. 3 shows the flowchart of the analysis of gas-phase formaldehyde. A gas phase containing formaldehyde is suctioned through a cartridge packed with silica gel coated with 2,4-dinitrophenylhydrazine (2,4-DNPH) by a pump, and is captured and derivatized in the cartridge. The resulting derivatives are then eluted from the cartridge with acetonitrile and subjected to the GC analysis.

■ Experiment

Gas samples with a formaldehyde concentration of approximately 1 or 10 ppm (v/v)* were prepared by capturing about 10 L of ambient air in a Tedlar® bag and injecting a formaldehyde aqueous solution with a micro syringe.

InertSep™ mini AERO series (GL Sciences Inc.) aldehyde sampler cartridge was used to trap and derivatize the compounds. Fig. 4 shows the gas capture and derivatization method. An ozone scrubber was used to remove atmospheric ozone in order to prevent decomposition of the DNPH derivatives. Two derivatization cartridges for formaldehyde capture were used in series, considering the possibility of breakthrough or other problems, and the cartridges were light-shielded during capture.

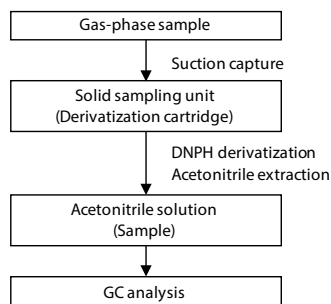* The concentration was calculated as an ideal gas.

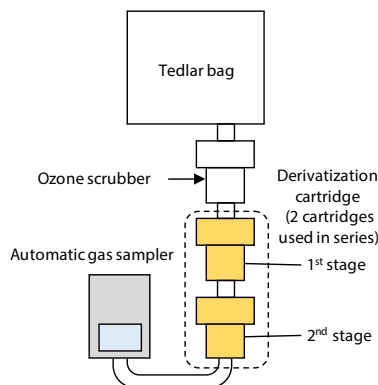**Fig. 3 Flowchart of Gas-Phase Formaldehyde Analysis**

Fig. 4 Schematic Diagram of Capture and Derivatization of Gas-Phase Formaldehyde

As depicted in Fig. 5 below, the derivatization cartridge and the ion exchange resin cartridge were connected in series, and the collected sample was eluted by slowly pumping 5 mL of acetonitrile through the derivatization cartridge. The ion exchange resin cartridge is necessary in order to remove any unreacted DNPH. Here, it may be noted that a solvent exchange of acetonitrile by ethyl acetate is necessary in the GC-FTD (Flame Thermionic Detector) method, considering the effect of a large amount of acetonitrile on the FTD detector (Application News No. G292). However, this additional extraction step is not necessary with the GC-FID method.
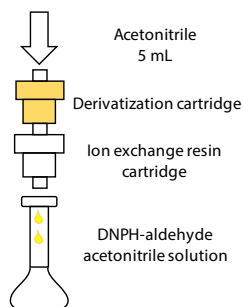

Fig. 5 Elution of DNPH-Formaldehyde

The three samples, as shown in Table 3, were prepared corresponding to the gas-phase formaldehyde concentrations and the number of cartridge stages. Blank was prepared by passing 5 mL acetonitrile through a derivatization cartridge without any suction capture of formaldehyde.

Fig. 6 shows the chromatograms of the three samples, and Table 3 shows the quantitation results for n=5. Samples ① and ② matched in the final quantitation results despite their difference in their original sample concentrations (Table 3). This is due to the absolute mass of formaldehyde collected in the trap cartridge being the same for both samples. The results for ③ confirmed that breakthrough does not occur in the 1st stage derivatization cartridge.

It should be noted that care is necessary when sampling formaldehyde with a concentration near the derivatization saturation limit under the condition of containing moisture, as the derivatization product may become unstable in some cases.
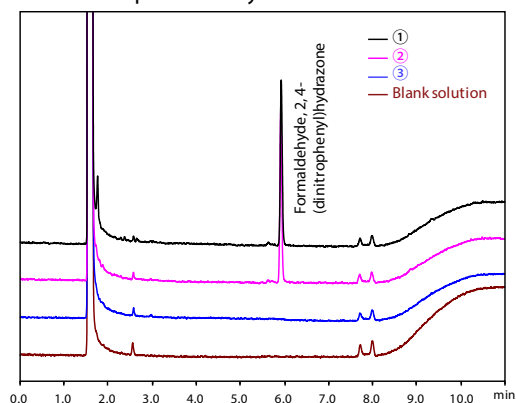

Fig. 6 Chromatograms of the three Samples (①, ②, ③) and Blank Solution

Table 3 Quantitation Results and Repeatability

No.	Gas-phase formaldehyde concentration ppm (v/v)	Captured amount L	Number of cartridge stages	Quantitative value ng/μL (Average of n=5)	Peak area repeatability RSD (%)
①	1	10 (approx.)	1	2.96	0.60
②	10	1	1	3.02	0.97
③	10	1	2	-	-

■ Conclusion

In this experiment, DNPH-derivatized samples of gas-phase formaldehyde were prepared and analyzed by the GC-FID method.

Using a DNPH-aldehyde standard sample, a calibration curve with a good linearity was prepared in the range of 1 to 100 ng/μL and good repeatability was confirmed at each calibration point. Good repeatability was also confirmed in a quantitative analysis of samples, which were prepared by DNPH derivatization of formaldehyde in atmospheric air (added formaldehyde concentration: approximately 1 or 10 ppm (v/v)).

Although HPLC, GC-FTD, or GC/MS is generally selected for analysis of DNPH-derivatized formaldehyde, analysis is also possible by GC-FID. On the other hand, because the detection sensitivity of GC-FID is low in comparison with GC-FTD and GC/MS, appropriate selection of the instrument to be used is necessary, the instrument selection depends at least partly on the concentration range of interest.

![SHIMADZU]

Shimadzu Corporation

www.shimadzu.com/an/