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Application News

No. G335A

Gas Chromatography

Quantitation of Hydrogen and Methane Dissolved in Hexanes, Toluene and Water

The amount of gases dissolved in a liquid solution may alter the functionality of the solution and affect the stability and reactivity of other dissolved components.

A high sensitivity detector is required for analysis of these gases as the amounts dissolved in a solution are generally at trace levels. Since inorganic gases are not detectable by the flame ionization detector (FID), the choice of the detectors is between the barrier discharge ionization detector (BID) and the thermal conductivity detector (TCD).

As BID possesses higher sensitivity compared to TCD and measures virtually all compounds with the exception of helium and neon, BID is the preferred detector for high sensitivity analyses of inorganic gases.

This article introduces analysis of hydrogen and methane in hexanes, toluene and water using the Shimadzu BID-2030.

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Sample Preparation

With hydrogen and methane as the target analytes, hexanes, toluene and water were used as the dissolving solutions in this experiment.

2 mL of the standard gas was taken into a 5 mL gas tight syringe while 2 mL of a liquid solution was aspirated into another 5 mL gas tight syringe. The two syringes were subsequently connected to each other.

The liquid solution was then transferred to the gas tight syringe containing the standard gas and then returned to its original syringe. The standard gas became dissolved in the solution as these steps were repeated five times. Despite the repetition, the solution was not saturated with the gases due to the surrounding air acting as contaminants.

Analysis Conditions

Table 1 below lists the instrument configurations and analytical conditions. The calibration curves were prepared by manually injecting the calibrator points, the preparation of which are discussed in the next section, using a 100 µL gas tight syringe. For the sample measurements, the samples were injected by an autosampler using an elastic syringe (P/N: 221-49548).

Table 1 Instrument Configuration and Analysis Conditions

Model	: Nexis™ GC-2030 / AOC-20i Plus
Injection volume	: 0.5 µL (autosampler: for solution measurement) 100 µL (manual injection: for calibration curve preparation)
Injection temp.	: 250 °C
Injection mode	: Split
Split ratio	: 1 : 5
Carrier gas	: He
Carrier gas control	: Constant linear velocity 50 cm/s
Purge gas	: 3.0 mL/min
Column	: SH-Msieve 5A (30 m × 0.53 mm I.D., d.f. = 50 µm) *1 (with 2.5 m particle trap)
Column temp.	: 40 °C
Detector	: BID-2030
Detector temp.	: 300 °C
Detector gas	: 50 mL/min

*1 P/N: 221-75763-30

Preparation of Calibration Curves

Gas samples at the concentrations of 10, 50, 100, 500, 1,000, and 5,000 ppm (v/v) were prepared by diluting the standard gases of hydrogen and methane with indoor air. Using a 100 µL gas tight syringe, 100 µL of each calibrator was injected into a gas chromatograph (GC) to establish a calibration curve. Figs. 1 and 2 are the calibration curves of hydrogen and methane respectively.

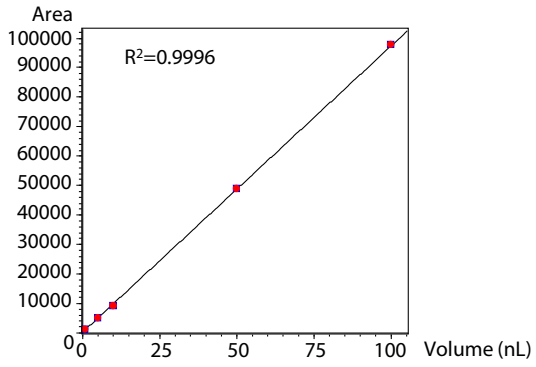

Fig. 1 Calibration Curve of Hydrogen (1, 5, 10, 50, 100 nL)

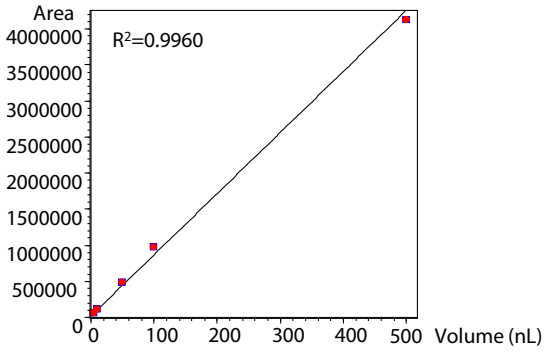

Fig. 2 Calibration Curve of Methane (5, 10, 50, 100, 500 nL)

Calculation of Repeatability and Quantitative Values

Repeatability (n = 5) and quantitative values were calculated using hexanes, toluene and water in which hydrogen or methane was dissolved. As one solution was switched to the next, the column was aged at 250 °C for 30 min in between. Fig. 3 and Fig. 4 are the chromatograms of hydrogen and methane dissolved in the three solutions. Table 2 lists the repeatability of the area values of hydrogen and methane in each of the solutions. Table 3 shows the quantitative results calculated based on the calibration curves in Figs. 1 and 2.

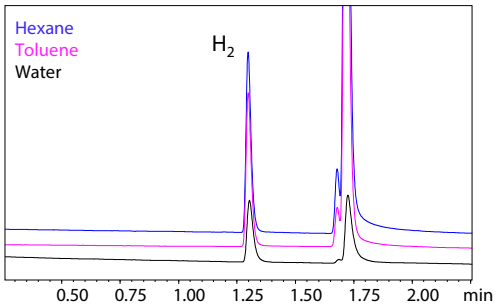

Fig. 3 Chromatogram overlay of Hydrogen dissolved in Hexanes, Toluene and Water

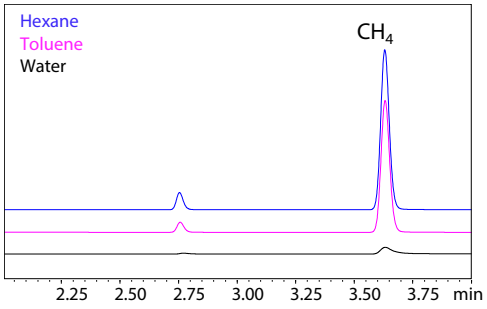

Fig. 4 Chromatogram overlay of Methane dissolved in Hexanes, Toluene and Water

Table 2 Repeatability of Area Values of the Gases Dissolved in Solutions (n = 5)

Gas	H_2			CH_4		
Solution	Water	Hexanes	Toluene	Water	Hexanes	Toluene
1st measurement	8386	20298	17616	186609	2543172	2123315
2nd measurement	8533	20406	17672	186681	2577628	2128268
3rd measurement	8004	20164	17577	182122	2587543	2115112
4th measurement	7826	19902	17492	179120	2589999	2083115
5th measurement	7589	20014	17503	178591	2580997	2051647
Average	8068	20157	17572	182625	2575868	2100291
%RSD	4.84	1.01	0.43	2.14	0.74	1.54

Table 3 Quantitative Values of the Gases Dissolved in Various Solutions

Gas	H_2			CH_4		
Solution	Water	Hexanes	Toluene	Water	Hexanes	Toluene
Volume (nL)	8.08	20.52	17.86	18.85	301.67	245.47
Quantitative value (nL/µL)	16.16	41.04	35.72	37.69	603.33	490.93
Quantitative value *1 (ng/µL)	1.32	3.36	2.92	24.66	394.80	321.25

*1 Calculated as an ideal gas at room temperature (25 °C).

Effect of Solution on Sample Integrity and Column During Analysis

To study the sample integrity during the course of this experiment, hydrogen dissolved in hexanes was continuously measured with the same sample. Fig. 5 depicts the downward drift in the area ratio with each injection, where the value 1 represents the area value normalized to that of the 1st measurement. The area values of hydrogen decreased over time and a similar tendency was also observed with the other solutions. This decrease was suspected to be caused by gas-liquid partition of the headspace atmospheric air inside the vial, allowing the target hydrogen to escape from the solution. Therefore, the use of a short measurement cycle was considered an effective countermeasure to improve reproducibility.

To study the column integrity, continuous measurements of methane dissolved in hexanes were conducted. Fig. 6 shows the shift in the retention time of methane as the number of measurements increased. As the number of measurements increased, an increasing amount of hexanes also remained in the column, resulting in shorter methane elution times. A similar tendency was also seen with the other solutions. In order to eliminate the solution from the column, aging was conducted at 250 °C for 30 min. This aging improved the consistency of the methane elution times.

Based on these observations, a short cycle measurement and a periodic aging of the column are deemed essential in the quantitation of hydrogen and methane in hexanes, toluene and water.

It should be noted that as the SH-Rt™- MSieve 5A used in this experiment is a column with extremely strong retention, the injected solution may easily remain in the column. Although some solutions are eliminated from the column by raising the column temperature, this may not be possible with others. The deterioration of repeatability and separation is possibly resolved by column trimming of ca. 50 cm. If the results do not improve with the cutting, it is necessary to change the column.

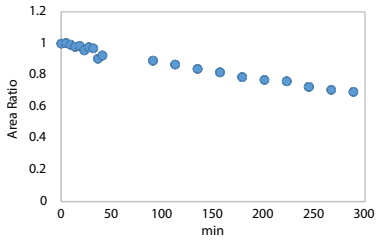

Fig. 5 Area Ratio Drift of Hydrogen in a Series of Injection

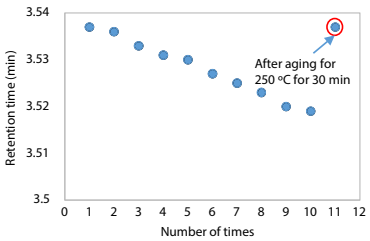

Fig. 6 Shift in Retention Time of Methane Over a Number of Measurements

Conclusion

Analysis of hydrogen and methane in hexanes, toluene and water using BID-2030 was conducted. Satisfactory repeatability of the area values of hydrogen and methane in the solutions was obtained with a short measurement cycle and a preriodic aging of the column.

BID-2030 is thus considered an excellent instrument in measuring the gases dissolved in liquid solutions.

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