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Abstract

This work describes development of a new spectrophotometric flow analysis technique suitable for monitoring of ethanol content in gasohol fuel. In this technique, the concept of membraneless gas-diffusion (MBL-GD) was applied with one-step aqueous extraction of gasohol (1:2 gasohol:water). Segments of aqueous extract and color developing reagent were allowed to flow into two separate channels in the MBL-GD device. Inside the device, ethanol vapor can diffuse across a small headspace between the two channels (donor and acceptor). Introduction of an air-segment behind the zone of acceptor reagent to stop dispersion of the colored zone has greatly improved the rapidity of analysis using this MBL-GD technique. Two methods were developed for quality control of gasohol by measuring ethanol content. Method I is suitable for direct calibration of E5 and E10. Method II is recommended for E20. These methods have high accuracy with good precision (% RSD: 1 to 4.9, n=45) and have a sample throughput of 26 samples h^{-1}. E10 samples were compared with analysis using a standard GC method.

Key words: Membraneless gas diffusion; flow-based; ethanol; gasohol.

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Introduction

Gasohol is a mixture of gasoline and ethanol with purity from 99.0 to 99.5 % (v/v). Ethanol is added to gasoline to supplement use of the fossil fuel. This type of alcohol-blended fuel has long been used in some countries such as in, Brazil, United States and Sweden. Gasohol was initiated in Thailand as one of the King's projects in the substitution energy program. Seventeen years later, after the beginning of the project, gasohol became available commercially at petrol stations throughout Thailand from 2002.

Ethanol is blended with gasoline at different percentages designated by an E-number which gives the percentage in volume of anhydrous ethanol that is blended with the gasoline base-fuel. The numbers indicate the percentage in volume of anhydrous ethanol that is blended with the gasoline base-fuel. Common percentages are E5, E10 and E20. For example, E5 contains ethanol at 5 % and gasoline at 95 %, by volume. Most modern automobiles are compatible with up to E10 without modifications. Some vehicles with specifically designed engines were made compatible with up to 85 % (v/v) ethanol (E85).

In making gasohol, the former octane enhancer, methyl tertiary butyl ether (MTBE), is no longer required. Ethanol acts as the octane booster for gasohol in addition to being the fuel substitute. Consequently, the ethanol content must be monitored closely to keep the octane number aligned with the standard. Generally in petrol industry, the monitoring is carried out at the production site and at the storage tanks, including the tanks at petrol stations.

ASTM D 4815-03 by gas chromatograph (GC) [1] is normally used for analysis of volatile ethers as well as alcohols including ethanol in gasoline. In this standard method, a complex arrangement of two different columns is required. A liquid mixed-mode chromatographic method (size-exclusion and affinity) with refractrometric detection has also reported by Zinbo from Ford Motor Company [2]. In addition, infrared methods have been developed and reported for quantitative analysis of ethanol in gasohol and in fuel ethanol, by using attenuated total reflectance (ATR) [3] and Fourier transform-near infrared (FT-NIR) [4], respectively.

Rocha *et al.* reported an impedance technique, for measuring ethanol content in ethanol-gasoline blends [5]. This system was strongly affected by the sample matrix. Paixão *et al.* reported use of amperometric detection on copper electrodes for the application in

gasohol samples [6]. This was formerly developed for use in determination of ethanol in beverages [7]. Flow analysis techniques have also been applied in method development for ethanol analysis. Alhadeff *et al.* reported some enzymatic methods using flow-based techniques for determination of ethanol contents in gasohol fuels [8, 9] and in fermentation bioprocess [10].

This paper reports the development of a new method for quantitative analysis of ethanol in gasohol. The previous design of a 'membraneless gas-diffusion' (MBL-GD) unit together with the indicator stream for colorimetric detection was adopted [11]. However, it was found that the unit and the operating procedure must be more specific to this gasohol application. Under new operating procedure with a modified unit configuration, analysis with MBL-GD concept is much improved in the terms of significant reduction in the signal tailing. In principle, the method in this paper should be more robust than use of the enzymes [8-10], and the method has a good potential in further development for making a portable device for quality control of gasohol.

Experimental

Chemicals and reagents

All chemicals used were analytical reagent grade. Solutions were prepared by dissolving the chemicals in distilled water.

Potassium dichromate (0.2 M $K_2Cr_2O_7$), employed as the acceptor stream, was prepared by dissolving 29.4 g of potassium dichromate crystal (Ajax, Australia) in 500 mL of 4 M sulfuric acid.

Preparation of working standard solutions

Method I: External calibration (suitable for E5 and E10)

Working standard solutions for Method I were prepared in distilled water by appropriate dilutions of standard ethanol (99.5 % (v/v) ethanol; Lab Scan, Ireland).

Method II: Calibration with standard extracts (suitable for E5, E10 and E20)

Working standard solutions for Method II were prepared by adding standard ethanol into gasoline base-fuel to obtain desirable concentrations. These standard solutions were then extracted with water using separatory funnel (1:2 gasohol:water is the optimum).

Sample preparation

Gasohol samples (5.00 mL) were used by extraction with water (10.00 mL) prior introduction into the flow system.

Membraneless gas diffusion unit

The MBL-GD unit was made similarly to that described in Choengchan *et al.* [11] using Perspex acrylic. However, the device was modified to improve some characteristics as described in results and discussions.

The flow system with micro-unit for MBL-GD

Fig. 1 is schematic diagram of the flow system with MBL-GD. The system was used for all experiments. The peristaltic pumps (Ismatec, Switzerland) were used with Tygon^{TM} pump tube (1.02 mm internal diameter) for propelling donor and acceptor streams. An Agilent diode-array spectrophotometer (Model 8453, Germany), equipped with a 40-mm flow-through cell (Hellma, Germany) was used as detector. The manifold in Fig. 1 was constructed by using 0.5 mm internal diameter PTFE tubing.

Results and discussion

Previous design and modifications

Manifold

The flow injection system reported by Choengchan *et al.* [11] was adopted with slight modification. The schematic diagram of the system is depicted in Fig. 1. Unlike the previous report, liquid sample was introduced to the flow system by time-based injection. Instead, the six-port injection valve was omitted as shown in Fig. 1, a switching valve (SV1) was used for sample introduction.

Accumulation of vapor inside the MBL-GD unit

Initially, a membraneless gas-diffusion unit with similar configuration to the one reported by Choengchan *et al.* [11] was constructed and used in the flow manifold (Fig. 1). The flow system was first tested using an aqueous ethanol solution (10 % (v/v) ethanol), and employed a similar operating scheme as described in the previous work. It was observed that

with the present dimension of the membraneless gas-diffusion unit (Fig. 2), the signal had a large tailing (Fig. 3a). The tailing of the signal like in Fig. 3a is a result of the increase in the depth of the groove made for the acceptor stream ('AS' in Fig. 2). For this work, the grooves of the membraneless gas-diffusion unit were made slightly deeper than the former unit [11]. Increasing the depth of the groove provides greater ease of control of the levels of donor and acceptor streams.

Modification of the MBL-GD unit for vapor release

In order to reduce the signal tailing, the MBL-GD unit was re-designed to have a new cover lid that has one side attached to the bottom piece containing the diffusion grooves or liquid channels (Fig. 2a). Unlike the former design [11], the lid can be opened or closed. While being closed, the MBL-GD unit is locked tightly during the process of gas-diffusion (from 'DS' to 'AS'). The lid can be opened easily with the new design to release the gas vapor from the unit.

Fig. 3b shows the results obtained from the modified unit with the open/closed lid. This demonstrated that signal tailing can be reduced by releasing the ethanol vapor from the headspace (the lid was opened after 3 min of diffusion time as per Step 3 in Table 1). The lid was kept opened until the signal returned to the baseline before it was closed for the next analysis.

Introduction of air segment: effective troubleshooting for the tailing

Although, the signal had less tailing with the release of the accumulated ethanol vapor, the analysis time was still long. Fig. 3b shows the analysis time was approximately 8 min injection^{-1}.

One possible cause of the persistent tailing in Fig. 3b could be the large degree of dispersion [12] in the 'AS' stream (Fig. 1). A change in configuration of the flow system, such as inserting a mixing coil may reduce the dispersion of reaction zone in the dichromate 'AS' stream, but may not be appropriate as this would unnecessarily increase the complication of the system.

In order to further reduce the tailing and to limit the effect of longitudinal dispersion, an air segment was introduced at the end of the AS stream. Fig. 4 was drawn schematically to present this scenario. As illustrated in Fig. 4, there was no air segment in the initial system (Fig. 4a), thus, the reaction zone is dispersed along the axis of the flow direction. The introduction of an air segment (Fig. 4b) resulted in limited dispersion of the reaction zone.

With the air segment introduced after the dichromate acceptor (Fig. 4b), no dispersion could take place at the tail of the acceptor zone (labeled as AC zone in Fig. 4). This resulted in major improvement in the tailing and a more acceptable signal profile as shown in Fig. 3c. A further benefit of insertion of the air segment in between analytical cycles was that the analysis time was reduced to 210 s injection^{-1}. For the calibration plot, a reading was taken exactly at 205 s from each profile (dotted area of Fig. 3c).

Fig. 3c shows a sharp rise of the profile just after 210 s, most likely due to the air segment passing through the flow-through cell. The sudden rise in the signal was the cause of the lens effect at the boundary between aqueous dichromate solution and the air.

Operating procedure of the manifold

In order to summarize the recommended operating procedure of the flow system in Fig. 1, Table 1 was constructed. The procedure described in Table 1 includes the steps of (i) vapor release and (ii) the insertion of air-segment to stop zone dispersion, which eliminate excessive tailing of signal. This procedure was designed in conjunction with use of the MBL-GD unit that has been modified to have the lid, optionally 'closed' or 'open' (Fig. 2).

Sample handling

Simple extraction using water

A preliminary study, using direct injection of gasohol into the manifold in Fig. 1 showed that the calibrations were not linear. There was a non-zero blank signal. This is most likely a matrix effect with volatile components from the gasohol interfering with the reaction. Thus direct analysis of gasohol is not appropriate using the MBL-GD described here. The matrix effects suggest that ethanol should be extracted prior to the analysis using the colorimetric flow analysis.

Studies were undertaken to determine percentage extraction of ethanol to water, of volume ratios at 1:1, 1:2 and 2:1 (gasohol:water). It was found, for synthetic E5 and E10 (5 % and 10 % (v/v) ethanol in base- fuel), that the extraction of up to 98 ± 2 % was obtained when using the volume ratio at 1:2 (gasohol:water). For gasohol samples, with greater in ethanol concentrations, percentage extraction (at the same volume ratio) decreased to 93 ± 2 % (E15) and 87± 2 % (E20). This suggested, for gasohol containing $\leq$ 10 % (v/v) ethanol, such as E5 and E10, that only single extraction step (1:2 gasohol:water) is adequate and the extract is

suitable for analysis using direct calibration method (Method I). However, for E20 or above, it is recommended that gasohol based standards be use for increased accuracy (Method II).

In this work, extraction of gasohol, using distilled water as extractant (1:2 gasohol: water) was used. For all gasohol samples (9 companies), separation between the two phases took no longer than 3 min after shaking in separatory funnel. After extraction, a gasohol extract can be analyzed by introduction into the donor stream (Fig. 1) using the scheme in Table 1.

System optimization

The conditions of the operation scheme (Table 1) and the flow system (Fig. 1) were optimized as described in the following sections.

Selection of diffusion path-length

Physical property of the MBL-GD unit was optimized by varying the length of the diffusion zone (AC zone in Fig. 4). Path lengths of 3, 5 and 7 cm were trialed. It was found that diffusion path-length at 3 and 5 cm provided inadequate sensitivities, consequently 7-cm was selected as the path-length since this length provided both satisfactory sensitivity and analysis time. It was also found that the levels of the DS and AS were controlled more easily with the 7-cm length than the shorter lengths.

Optimization of flow rate

The flow rate of acceptor stream is an important parameter which controls the sensitivity and sample throughput in flow analysis. In this case, the flow rate of donor stream should have a negligible effect on these two parameters. Nevertheless, the two streams were operated at equal flow rates for ease of operation. Calibration slope dropped significantly when the flow rate changed from 1.4 to 2.4 mL min^{-1} which equates to 14 samples h^{-1} (at 1.4 mL min^{-1}) to 26 samples h^{-1} (at 2.4 mL min^{-1}). By considering sensitivity and analysis time, the flow rate of 2.0 mL min^{-1} was selected to give a sample throughput of 24 samples h^{-1}.

Diffusion time

Diffusion time is the interval time of step 3 in Table 1, at which the zone of dichromate reagent ('AC zone' in Fig. 4) was rested inside the MBL-GD unit together with the rested sample zone. During this period, the flow was paused to achieve adequate collection of the volatile chemical product in the 'AC zone'. Practically, the flows of donor and acceptor are

paused while gasohol extract is inside the MBL-GD unit. In order to obtain the desirable sensitivity and sample throughput, the diffusion time was investigated at 1, 3, 5 and 7 min. As expected, the sensitivity (calibration slope) increased with increasing diffusion time. The longer the diffusion interval, the more colored product was obtained from increasing in the quantity of diffused ethanol vapor. For this work, 1 min was chosen as the optimum time due to fast sample throughput (26 samples h^{-1}) and its satisfactory in the sensitivity.

Aspirated volumes of acceptor stream and of sample extract

It is recommended that introduction of an air segment behind the 'AC zone' (Fig. 4) is necessary to limit the zone dispersion in the dichromate-acceptor stream. The length of air segment determines the length of the acceptor stream or the total volume of acceptor solution in one cycle. The length of acceptor stream was investigated to find the optimum value.

The length of acceptor stream is a measure of the length of dichromate solution (in the tube), starting from the front of air segment to the position of flow-through cell. Lengths of 69, 80 and 88 cm were investigated which resulted in the volume of dichromate solutions of 1.78, 1.87 and 1.94 mL, respectively (each includes the volume inside the MBL-GD = 1.22 mL). This was done to minimize the length of dichromate solution in the lines leading to the detector unit and subsequently minimize the extent of dispersion in the stream.

Fig. 5 illustrated that the signal height increased as the length of dichromate acceptor was shorter. The analysis time decreased significantly (peak became narrower) with decreasing in the length of acceptor. 69 cm was chosen as the optimum length giving an acceptor stream length of approximately 1.78 mL per cycle.

The volume of sample (aqueous extract of gasohol) that is introduced into the system should not be critical so long as there is enough sample to fill the full 7-cm length of the MBL-GD unit. According to step 2 in Table 1, 1.33 mL of sample extract was introduced for each analysis.

The optimum condition and performance

The selected condition for the flow system in Fig. 1 used in this study has been summarized in Table 2. Performance of the developed method was examined accordingly to the features appearing in the Table 3.

Table 3 shows the two methods developed for the flow system. For E5 and E10 samples, method I is strongly recommended due to its convenience from direct calibration with aqueous standards. Only one step of aqueous extraction is required for this method since

percentage extraction for E5 and E10 were close to 100 %. For users that have types of gasohol including E20, method II (Table 3) is preferable due to the decreased percentage extraction when the ethanol content is greater than 15 % (v/v), with 1:2 extraction ratios (gasohol:water).

The developed method provides a reasonable throughput of sample with acceptable precision. The method provides a detection limit for ethanol down to approximately 1 % (v/v) in gasohol.

This method has been compared with the ASTM method [1]. Table 4 shows the comparison between the analyses by the MBL-GD method and the ASTM method. Using paired *t*-test the results of the two methods are not significantly different (t_{stat} = 2.26, $t_{critical}$ = 2.31 at 95 % confidence) [15].

Conclusion

This work presents new and alternative technique for measuring ethanol in gasohol. The technique is simple but providing equivalent accuracy and precision with the GC-ASTM method [1] (Table 4). Based on the developed technique, two methods are available and method selection depends upon the degree of ethanol that is blended to gasoline base-fuel. Above 10 % (v/v), such as commercial E20, it is advisable to carry out extraction of samples as well as the standards (Method II). However for more common blend, such as E10 (or below), extraction is necessary only for samples, with external calibration with standard ethanol prepared in water (Method I).

Compared to GC, the technique is simpler and more cost effective than GC. Although the colorimetric detection method is not specific for ethanol vapor, the selectivity of the technique is ensured by liquid-liquid extraction with distilled water. This method also has the advantage of being more portable than the GC method and has the potential to be used on-site.

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Figure Captions

Fig. 1 The flow system with membraneless gas-diffusion (MBL-GD) unit for determination of ethanol using colorimetric detection. DS, donor stream (water); AS, acceptor stream (dichromate in sulfuric acid solution); SV1, switching valve for donor stream; SV2, switching valve for acceptor steam; P1, peristaltic pump for donor stream; P2, peristaltic pump for acceptor stream; D, Spectrophotometer.

Fig. 2 The membraneless gas-diffusion unit employed for quantitative analysis of ethanol in gasohol.

Fig. 3 Signal profiles obtained from 1.22 mL injections of 10 % (v/v) ethanol in water; (a) closed MBL-GD with no air-segment (former design, [Ref. 11]); (b) lid (of MBL-GD) opened at 3 min, and no air-segment and (c) lid (of MBL-GD) opened at 3 min with 0.34 mL of air-segment.
Note: Air-segment was introduced at the end of AC zone as shown in Fig. 4

Fig. 4 Illustration of system operation for one analytical cycle using (a) the continuous acceptor stream of dichromate solution and (b) the non-continuous acceptor stream with an air segment. AS: acceptor stream; DS: donor stream; SV1: switching valve in donor stream; SV2: switching valve in acceptor stream; AC zone: acceptor zone; MBL-GD unit: membraneless gas-diffusion unit.

Fig. 5 Signal profiles obtained using three different volumes of acceptor streams. Acceptor stream: 0.2 M $K_2Cr_2O_7$ in 4.0 M H_2SO_4. Test solution: 20 %(v/v) ethanol in H_2O. MBL-GD: 7-cm path length. Flow system: same as in Fig. 1.

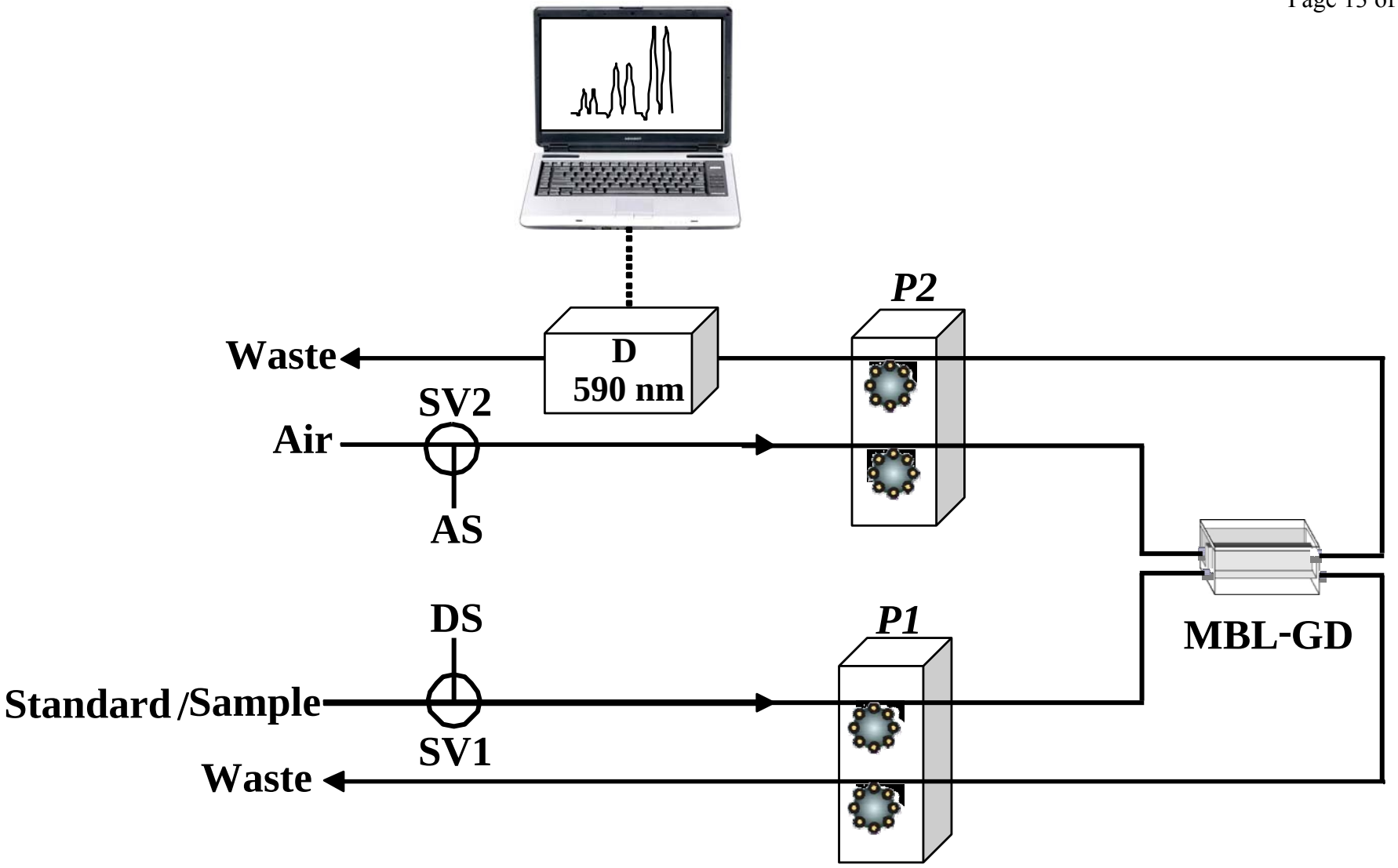
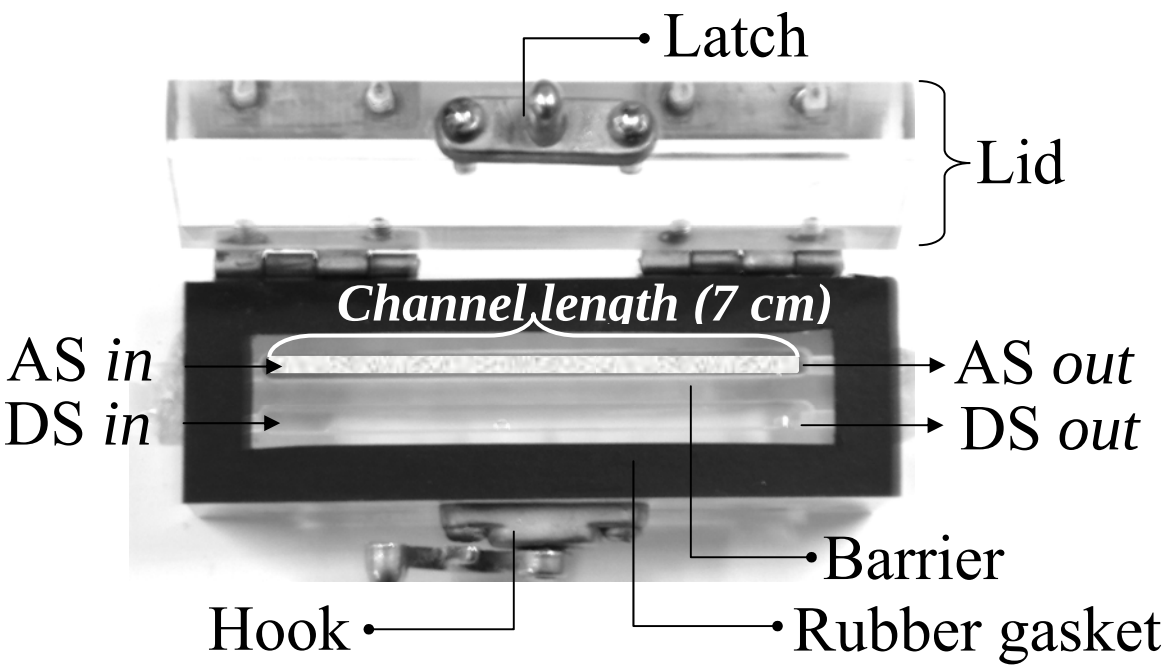

P2
Waste
D
590 nm
SV2
Air
AS
MBL-GD
DS
P1
Standard /Sample
SV1
Waste

Fig. 1

a. Top view



b. Side view

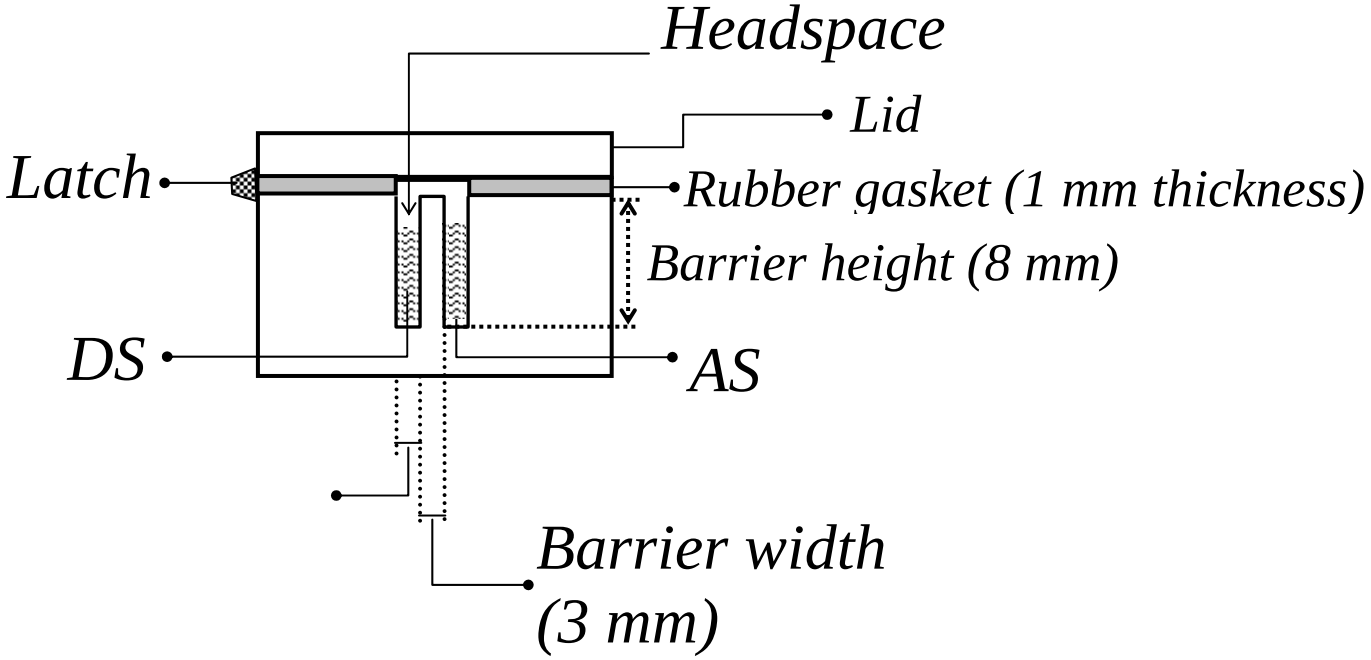


Fig. 2

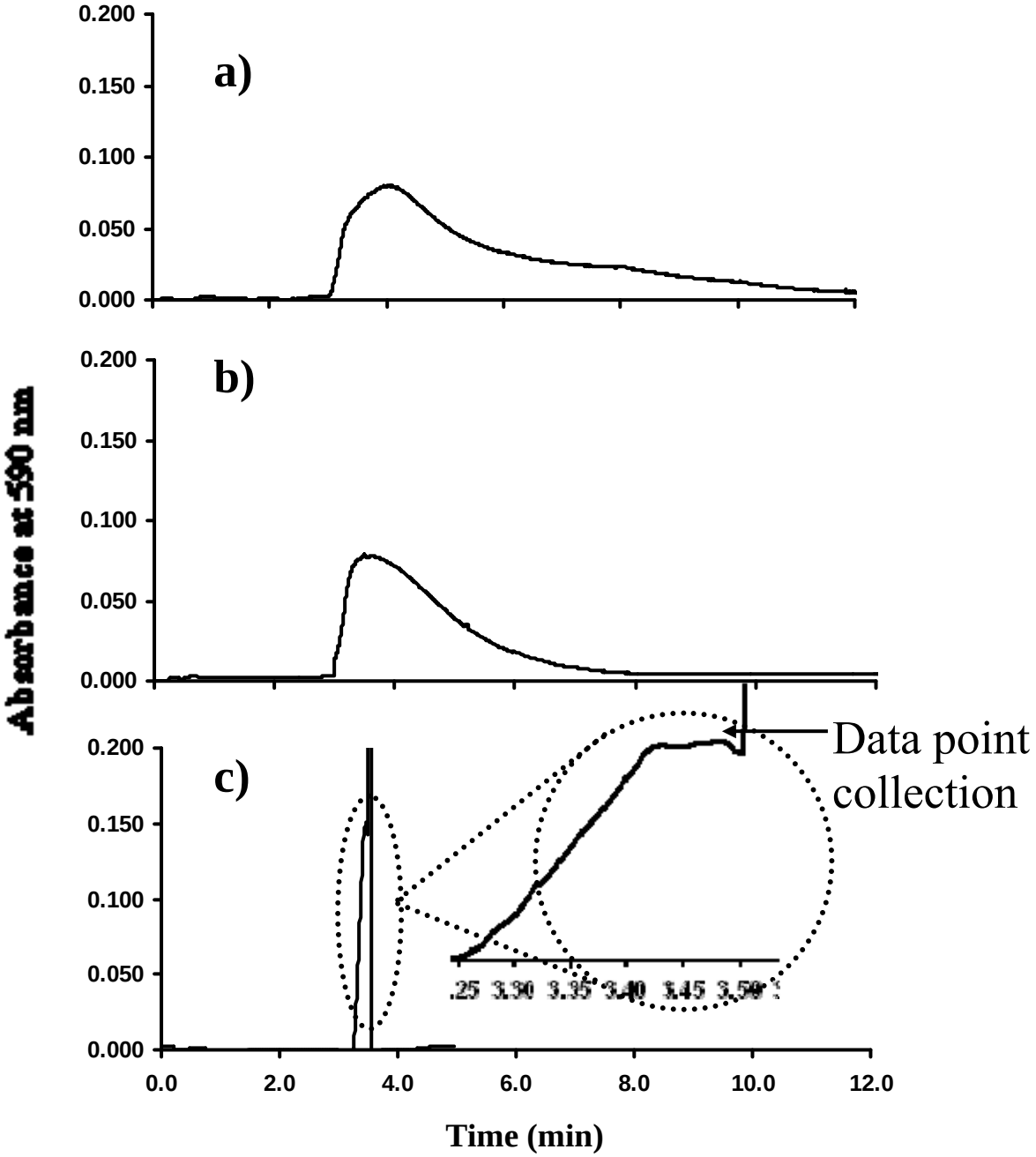

a)
b)
c)
0.200
0.150
0.100
0.050
0.000
Absorbance at 590 nm
Data point collection
.25 3.30 3.35 3.40 3.45 3.50
0.0
2.0
4.0
6.0
8.0
10.0
12.0
Time (min)

Fig. 3

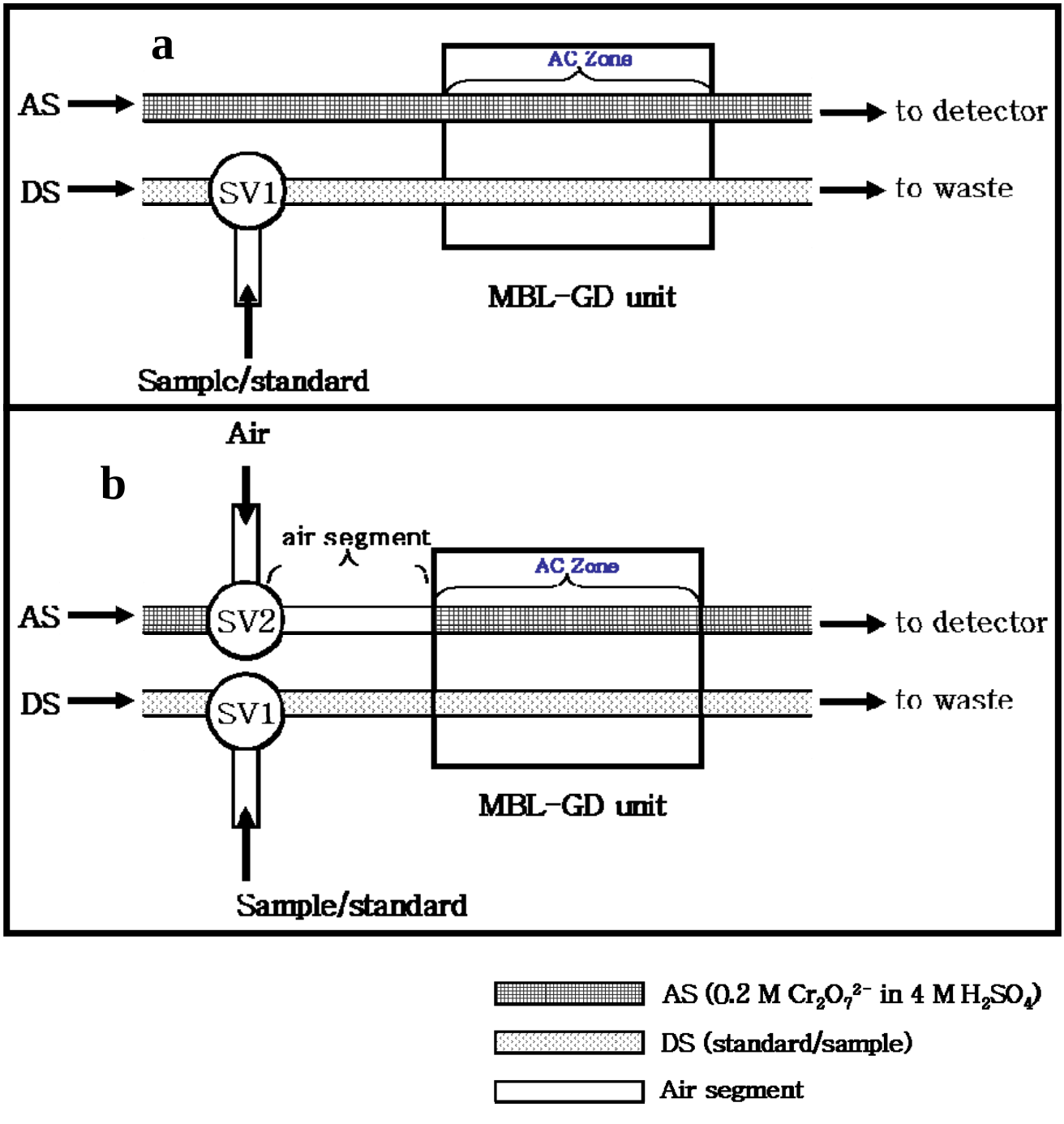

a
AC Zone
AS
to detector
DS
SV1
to waste
MBL-GD unit
Samplc/standard
Air
b
air segment
AC Zone
AS
SV2
to detector
DS
SV1
to waste
MBL-GD unit
Sample/standard
AS (0.2 M $Cr_2O_7^{2-}$ in 4 M H_2SO_4)
DS (standard/sample)
Air segment

Fig. 4

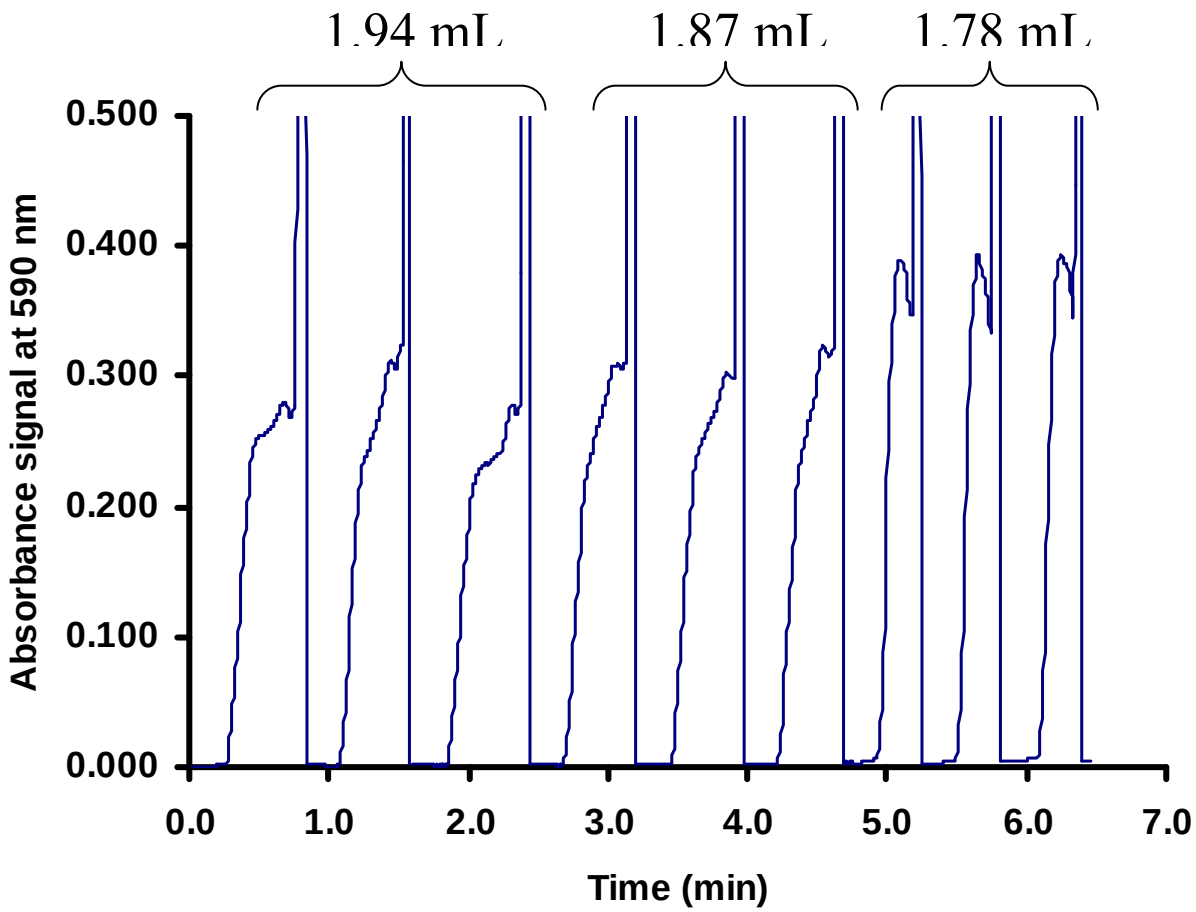

1.94 mL
1.87 mL
1.78 mL
0.500
0.400
0.300
0.200
0.100
0.000
Absorbance signal at 590 nm
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Time (min)

Fig. 5

Table 1 Operation of the flow system in Fig. 1 with MBL-GD for quantitative analysis of ethanol in gasohol.

Step	Operation	Pump		Valve position		Lid	Duration
		P_1(DS)	P_2(AS)	SV1(DS)	SV2(AS)	(MBL-GD)	(s)
0	Reagents filling (prior to analysis)	ON	ON	H_2O	RE	OPEN	60-90
1	Air introduction to AS	OFF	ON	H_2O	AIR	OPEN	10
2	Sample introduction to DS	ON	OFF	S	RE	CLOSED	40
3	Gas-diffusion in stopped-flow mode	OFF	OFF	H_2O	RE	CLOSED	Selectable 'diffusion time' (e.g., 60, 180, 300 and 420)
4	Vapor release and flushing	ON	ON	H_2O	RE	OPEN	40

RE: Reagent (dichromate in sulfuric acid)
S: Sample or standard ethanol solution

Table 2 Recommended condition of the MBL-GD flow system in Fig. 1 (operated under the scheme in Table 1) for quantitative analysis of ethanol in gasohol by single aqueous extraction.

Parameter	Selected condition
1. Diffusion path-length	7 cm
2. Flow rate of donor and acceptor streams	2.0 mL/min
3. Diffusion time	1 min
4. Aspirating volume of dichromate per cycle	1.78 mL
5. Aspirating volume of sample (aqueous gasohol extract) per cycle	1.33 mL
6. Concentration of dichromate in AS	0.2 M
7. Concentration of sulfuric acid in AS	4 M

Table 3 Analytical performance of the developed flow system with MBL-GD unit for selective determination of ethanol in gasohol using single aqueous extraction (1:2 gasohol:water).

Feature	Performance	Remark
(1) Method I: External calibration		
1.1 Recommended calibration range (% (v/v) ethanol in gasohol	3 to12	- Calibration is made from aqueous standard.
1.2 Example calibration and correlation coefficient	$Y = 5.60 \times 10^{-2}$ ($\pm 2.13 \times 10^{-3}$)$X + 1.14 \times 10^{-2}$($\pm 2.46 \times 10^{-2}$) (r^2=0.996)	- Suitable for E5 and E10 by single aqueous extraction.
(2) Method II: Calibration with standard extracts		
2.1 Linear calibration range (% (v/v) ethanol in gasohol)	3 to 80	- Calibration is made from aqueous extraction.
2.2 Example calibration and correlation coefficient	$Y = 7.72 \times 10^{-2}$ ($\pm 1.00 \times 10^{-3}$)$X + 3.80 \times 10^{-3}$($\pm 1.15 \times 10^{-2}$) (r^2=0.996)	- Suitable for E5, E10 and E20, all by single aqueous extraction.
(3) Limit of detection (3SD of blank/slope) (% (v/v) ethanol in gasohol)	0.9	Method I & II
(4) Throughput (sample/h)	26	Method I & II
(5) Precision (% RSD of 10% (v/v) ethanol in gasohol n= 45)	1 to 4.9	Method I & II

260 **Table 4** Comparison of the ethanol concentration in gasohol samples, determined by the MBL-GD coupled to flow system and by the GC method (ASTM D 4815-03 [1]).

Sample	Ethanol concentration (% v/v)	
	MBL-GD (mean ± SD, n = 5)	**GC (mean ± SD, n = 3)**
S1	9.7 ± 0.3	9.7 ± 0.1
S2	9.8 ± 0.3	9.2 ± 0.2
S3	9.4 ± 0.5	9.5 ± 0.4
S4	8.9 ± 0.4	9.0 ± 0.4
S5	9.2 ± 0.3	9.0 ± 0.3
S6	9.6 ± 0.1	9.1 ± 0.3
S7	8.9 ± 0.4	8.6 ± 0.5
S8	9.2 ± 0.4	8.9 ± 0.5
S9	8.7 ± 0.3	8.8 ± 0.3