Chapter 3

RESULTS AND DISCUSSION

This study focused on the analysis of acetaldehyde residue in newly blown Polyethylene Terephthalate (PET) bottles by gas-liquid chromatographic technique (GLC) using helium as the mobile phase and DB-1, 100% dimethylpolysiloxane capillary column (15 m × 0.53 mm I.D. × 3 μm film thickness) as the stationary phase. The flame-ionization detector was used for acetaldehyde detection. It was necessary to optimize the analysis conditions for the best GLC performance.

3.1 Optimization of the GLC-FID analysis conditions

3.1.1 Carrier gas (He) flow rate

The optimum carrier gas flow rate was determined by considered its effect on the height equivalent to a theoretical plate (*HETP*) as shown in the van Deemter equation.

$$HETP = A + B/\mu + C\,\mu \qquad (1)$$

Where A = Eddy diffusion term: a constant that accounts for the effect of "eddy" diffusion in column

= $2\lambda d_p$; λ is a factor characteristic of the packing and d_p is the particle diameter of the packing

B = longitudinal diffusion term: a constant that accounts for the molecular diffusion of the vapor in the direction of the column axis

= $2\lambda D_g$; D_g is the diffusion coefficients of the component in gas Phase

C = mass transfer term: a constant proportional to the resistance of the column packing to mass transfer of solute through it

= $(8/\pi^2)[k'/(1+k')^2](d_f^2/D_l)$; k' is the capacity ratio, d_f is the effective thickness of the liquid film on the support and D_l is the diffusion coefficients of the component in the liquid phase

μ = the linear velocity of carrier gas (mobile phase)

In this research, a 15 m wall- coated open tubular (WCOT) column (0.53 mm i.d.) was used. In this column, a liquid phase is coated on fused silica wall with no packing material, therefore, the A term is nonexistent because there is only one flow path and no packing material. The resistance- to- mass-transfer term C has the greatest effect on band broadening, and its effect in capillary columns is controlled by the mass transfer in the gas phase C_G (Grob, 1985). For capillary columns, equation 1 takes a different form, and this is known as the Golay equation where

$$HETP = B/\mu + C_G \mu \qquad (2)$$

The above equation showed that *HETP* is proportional to the flow rate of carrier gas (μ). It is also known that an optimum carrier gas flow rate will give an optimum column resolution with the narrowest *HETP* (Grob, 1985)

Equation (1) shows the dependence of *HETP* on carrier gas flow rate and represented a hyperbola with its minimum at velocity $\mu = \sqrt{B/C}$, and the minimum *HETP* value $HETP_{min} = A + 2\sqrt{BC}$ (Szepesy, 1970). The change in *HETP* versus average linear velocity of carrier gas is shown in Figure 14.

The plate theory assumes that the column is divided into a number of zones called "theoretical plates" and called "*HETP*" as the zone thickness. These terms was used to define the column efficiency according to the equation

$$HETP = \frac{L}{N} \qquad (3)$$

where L is length of the column in centimeters and N is the number of theoretical plates.

The column efficiency improved with an increase in number of theoretical plates or decrease in *HETP* that corresponded to van Deemter equation. In practice it was difficult to achieve the terms B and C in equation (2), then equation (3) was then used to calculate the *HETP*.

The number of theoretical plates (N) could determine by equation (4)

$$N = 16 \left(\frac{t_R}{W} \right)^2 \qquad (4)$$

where t_R is the retention time of the peak *and* W is the base width of the peak.
The other generally used expression to calculate the number of theoretical plates is:

$$N = 5.54 \left(\frac{t_R}{W_{0.5}} \right)^2 \qquad (5)$$

where $W_{0.5}$ is peak width at half-height.

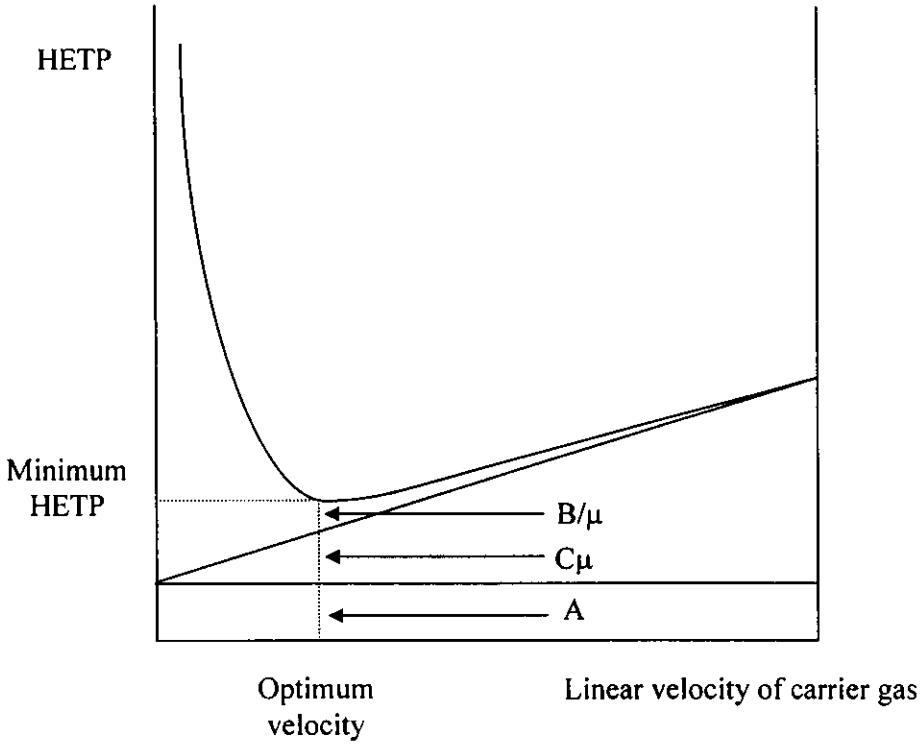


Figure 14 The van Deemter plot

The characteristic data of the elution peak are illustrated in Figure 15. In this study, a capillary column was employed, and sharp peaks were obtained. Therefore it is difficult to determine the base peak width. Thus, the number of theoretical plates can be calculated directly from the value obtained from a chromatogram as shown in Figure 15 by the relationship

$$N = 2\pi (t_R h / A)^2 \qquad (6)$$

where t_R is the retention time, h is integral peak height and A is integral peak area (Grob, 1985).

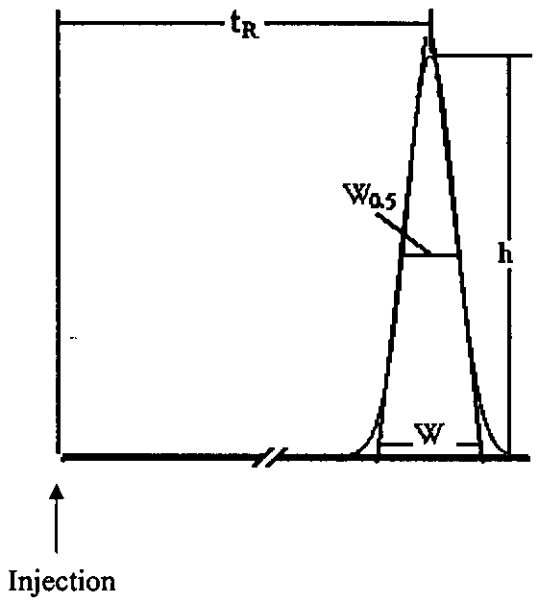


Figure 15 Characteristic data of the elution peak

The experiment to find optimum carrier gas flow rate (He) was carried out and the results are shown in Table 2 and Figure 16. The flow rate of 8.0 mL min^{-1} was obtained as the optimum since it gave the lowest *HETP* from the van Deemter plot (Figure 16).

Table 2 Height equivalent to a theoretical plate (*HETP*) of acetaldehyde (0.25 mL, 0.34 μg mL^{-1}) at various carrier gas flow rates

Flow rate (mL min^{-1})	*HETP* (mm)*
7.5	0.240 ± 0.006
8.0	0.230 ± 0.004
8.5	0.26 ± 0.01
9.0	0.28 ± 0.01
9.5	0.27 ± 0.01

* 4 replications, RSD < 4%

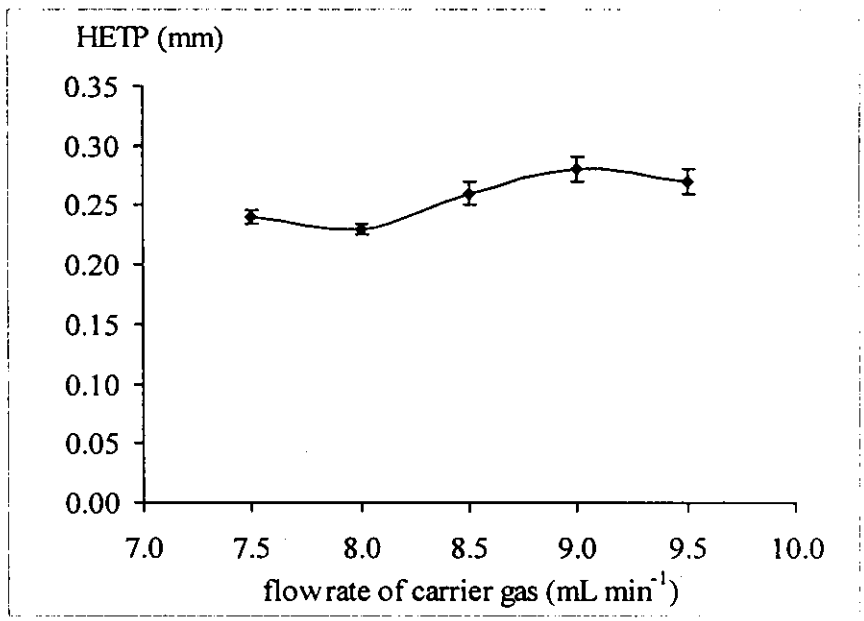


Figure 16 The van Deemter plot of acetaldehyde

3.1.2 Column temperature

The column temperature is one of the important parameters in gas chromatography technique since it could minimize time used for analyte elution, increasing detectability and reducing analysis time. The column temperature was performed on the isothermal mode (Baugh, 2002). The optimum column temperature (2.5.2) was obtained by considering the response and analysis time.

The results (Table 3 and Figure 17) indicated that the response increased as the column temperature increased, while the analysis time decreased. However, the lifetime of column would decrease as the column temperature increased. Therefore, to prolong the lifetime of the column, *i.e.,* the stationary phase, the optimum column temperature should be lower than the maximum temperature of the stationary phase, *i.e.,* 260 °C. Since between 130 and 170 °C, the percentage of difference response was lower than 10%, thus, the optimum column temperature was then taken as 130 °C.

3.1.3 Detector temperature

The detector temperature was optimized by considering the sensitivity. The results are shown in Table 4 and Figure 18. The relationship between detector temperature and the response indicated that the response increased with temperatures. The highest response was obtained at 270 °C. Thus, the optimum detector temperature was 270 °C.

Table 3 Response and analysis times of 0.34 μg mL^{-1}, 0.25 mL acetaldehyde at various column temperatures

Temperature (°C)	Response ($\times 10^3$)*, pA	Analysis time (min)
40	7.33 ± 0.05	0.94
50	8.0 ± 0.21	0.89
60	8.81 ± 0.14	0.86
70	9.68 ± 0.25	0.83
80	9.73 ± 0.38	0.80
90	10.53 ± 0.25	0.78
100	10.40 ± 0.28	0.76
110	11.37 ± 0.15	0.75
120	10.99 ± 0.26	0.73
130	12.01 ± 0.25	0.73
140	11.78 ± 0.21	0.71
150	12.02 ± 0.40	0.70
160	12.13 ± 0.14	0.69
170	12.22 ± 0.42	0.68

* 4 replications, RSD < 4%

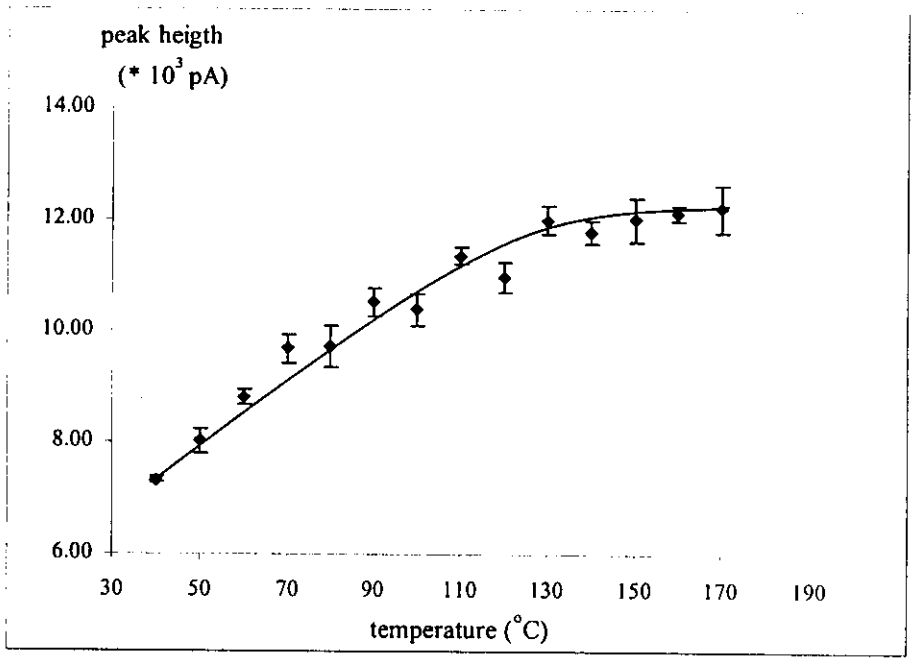


Figure 17 Response *versus* column temperatures of acetaldehyde 0.25 mL, 0.34 μg mL^{-1}

Table 4 Response of 0.34 μg mL^{-1}, 0.25 mL acetaldehyde standard gas at difference detector temperature

Temperature (°C)	Response ($\times 10^3$)*, pA
240	11.89 ± 0.46
250	11.72 ± 0.30
260	12.52 ± 0.45
270	12.91 ± 0.46
280	12.51 ± 0.23

* 4 replications, RSD < 4%

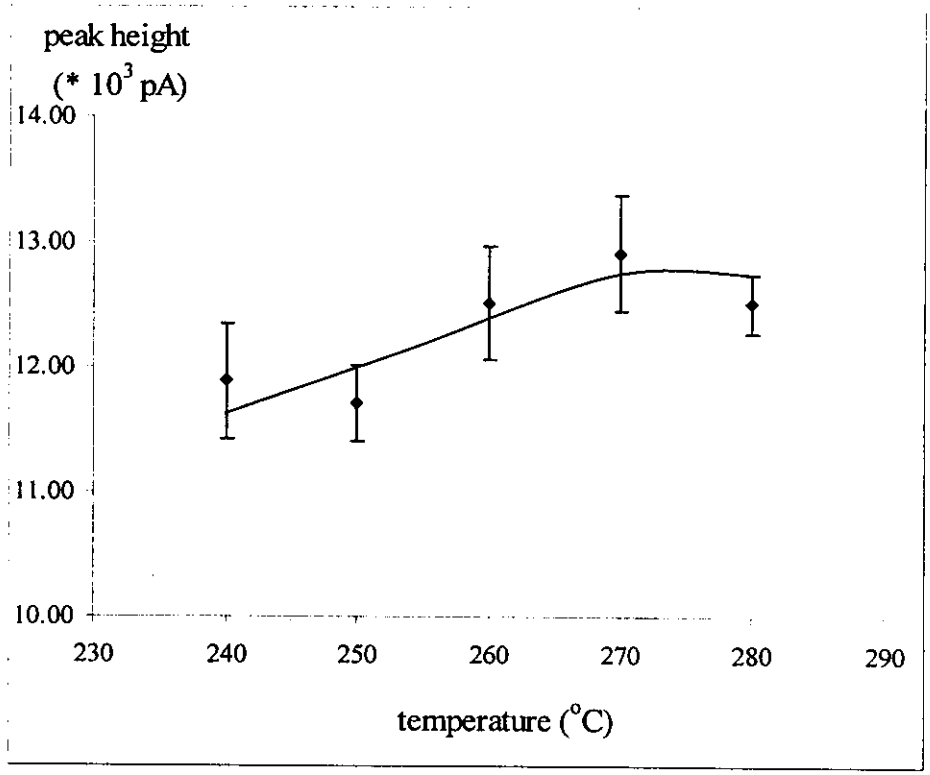


Figure 18 Response *versus* detector temperature of 0.34 μg mL^{-1}, 0.25 mL acetaldehyde

3.1.4 Valve temperature (injector temperature)

In gas chromatography technique the injector must be set at a higher temperature than the boiling point of the analyte in order to change the sample phase from liquid to vapor at the injector. However, in this study, the analyte was already equilibrated into the gas phase before being introduced to the gas chromatography. Therefore, the analysis could be achieved at a low injector temperature. This should be lower than the maximum temperature allowed for the gas sampling valve that was integrated to the injector 225 °C. Therefore, the injector was optimized in the range between 120 and 180 °C and the results are shown in Table 5 and Figure 19. The highest response was obtained at 140 °C. Thus, the optimum injector temperature was 140 °C.

Table 5 Response of 0.34 μg mL^{-1}, 0.25 mL acetaldehyde standard gas at difference valve temperature

Temperature (°C)	Response ($\times 10^3$)*, pA
120	11.78 ± 0.25
130	12.64 ± 0.33
140	13.07 ± 0.20
150	12.91 ± 0.26
160	12.46 ± 0.48
170	11.48 ± 0.43
180	11.60 ± 0.20

* 4 replications, RSD < 4%

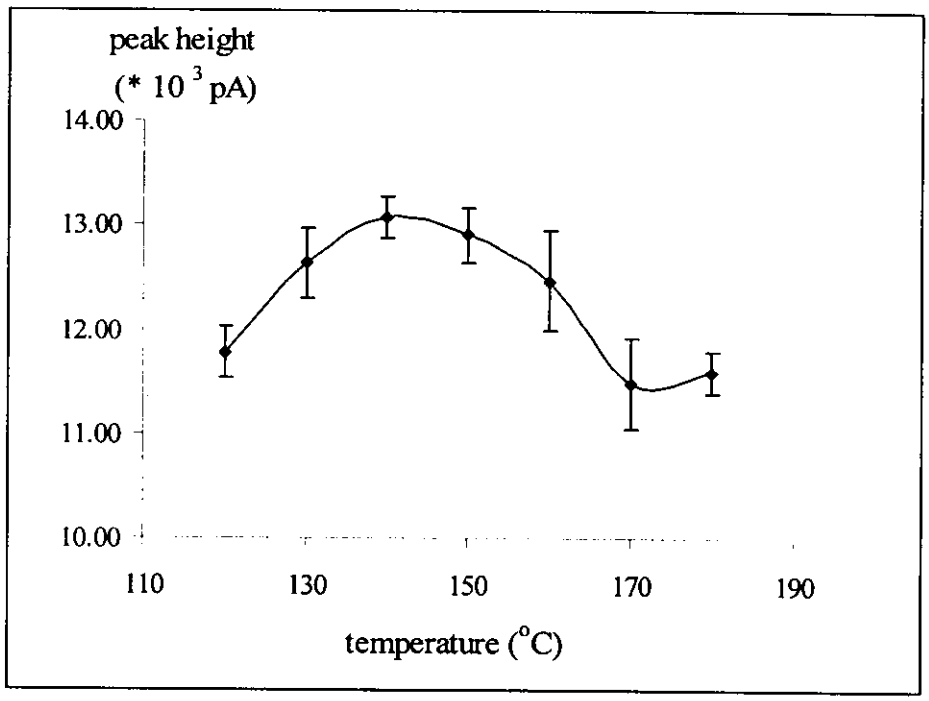


Figure 19 Response *versus* valve temperature of 0.34 μg mL^{-1}, 0.25 mL acetaldehyde

3.1.5 Fuel (hydrogen) flow rate

The analyte that was eluted from the column would be detected by flame ionization detector (FID). This detector consisted of a small hydrogen-air diffusion flame burning produced from oxidant and fuel gas. The oxidant gas was air and the fuel gas was hydrogen. Thus, the flow rate of air and hydrogen would significantly influence the noise level and the sensitivity of the detector.

Table 6 and Figure 20 show the effect of hydrogen flow rate where the highest response, *i.e.*, the optimum was obtained at 30 mL min^{-1}. This value agreed with Szepesy (1970) where the adequate value of hydrogen flow rate was found at 15-50 mL min^{-1}.

Table 6 Response of acetaldehyde 0.25 mL, 0.34 μg mL^{-1} at difference hydrogen flow rate

Flow rate (mL min^{-1})	Response ($\times 10^3$)*, pA
25	10.61 ± 0.27
30	13.07 ± 0.20
35	11.12 ± 0.17
40	11.13 ± 0.29

* 4 replications, RSD < 4%

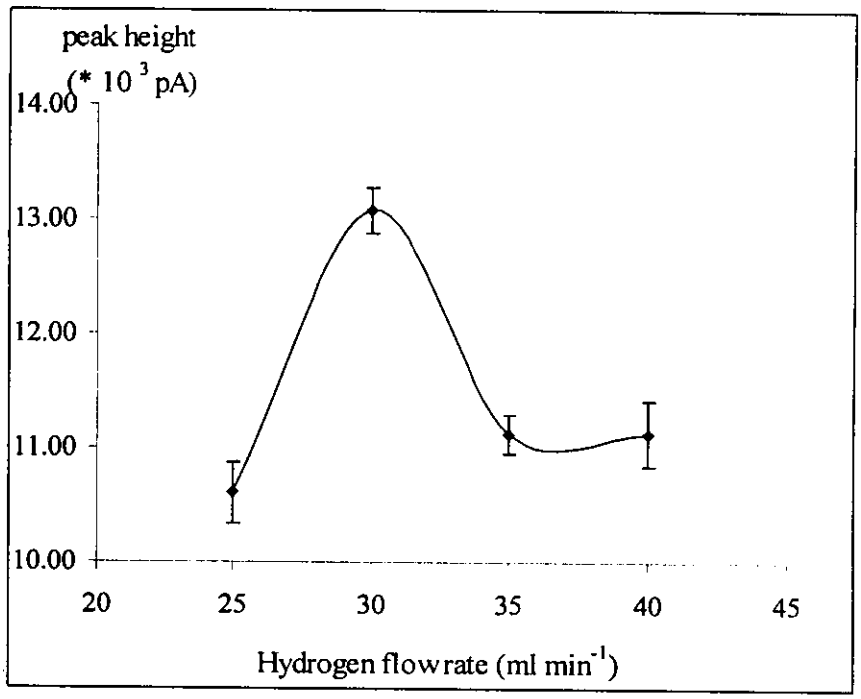


Figure 20 Response *versus* hydrogen flow rate of acetaldehyde 0.25 mL, 0.34 μg mL^{-1}

3.1.6 Oxidant gas (air) flow rate

The effect of the oxidant gas flow rate was studied (2.5.6) and the optimum of 300 mL min^{-1} was obtained from Table 7 and Figure 21, because it gave the highest response. Therefore, the optimum flow rate ratio of fuel and air was 1:10 and this agreed well with most GC-FID systems (Poole and Schuette, 1984).

Table 7 Response of acetaldehyde 0.25 mL ,0.34 μg mL^{-1} at difference air flow rate

Flow rate (mL min^{-1})	Response ($\times 10^3$)*, pA
250	10.61 ± 0.27
300	13.07 ± 0.20
350	11.12 ± 0.17
400	11.13 ± 0.29

* 4 replications, RSD < 4%

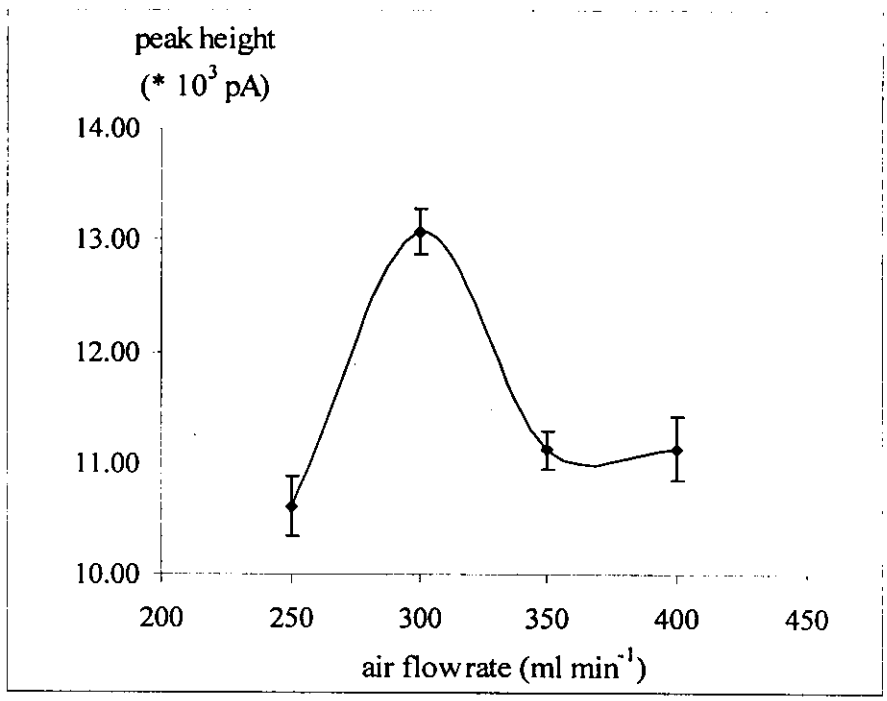


Figure 21 Response *versus* air flow rate of acetaldehyde 0.34 μg mL^{-1}, 0.25 mL

3.1.7 Make up gas flow rate

FID requires a make up gas to carry the analyte in the column to the detection zone. Lighter carrier gas (He) can operate at a relatively low flow rate (8.0 mL min^{-1}), and a make up gas is added to the stream just before it enters the detector. The addition of this gas provides the high flow rate that match the detector requirement. Without the make up gas, the analyte will be delayed at the end of the column because the volume of gas that flow through the column is not sufficient to drive it through the relative large volume of the detector (Greenlief, 2001).

In this study, nitrogen was used as additional make up gas and its flow rate was optimized for high sensitivity (2.5.7). The results are shown in Table 8 and Figure 22. The highest response of acetaldehyde was obtained at 20 mL min^{-1} for the gas sampling valve system. This condition agreed with the rate recommended by the manufacture, *i.e.*, the make up gas flow rate should be in the range of 10 to 40 mL min^{-1}, and the suggested flow is 20 mL min^{-1}.

Table 8 Response of acetaldehyde 0.25 mL, 0.34 μg mL^{-1} at various nitrogen flow rate

Flow rate (mL min^{-1})	Response ($\times 10^3$)*, pA
10	7.99 ± 0.11
20	10.85 ± 0.31
30	9.00 ± 0.45
40	6.60 ± 0.25

* 4 replications, RSD < 4%

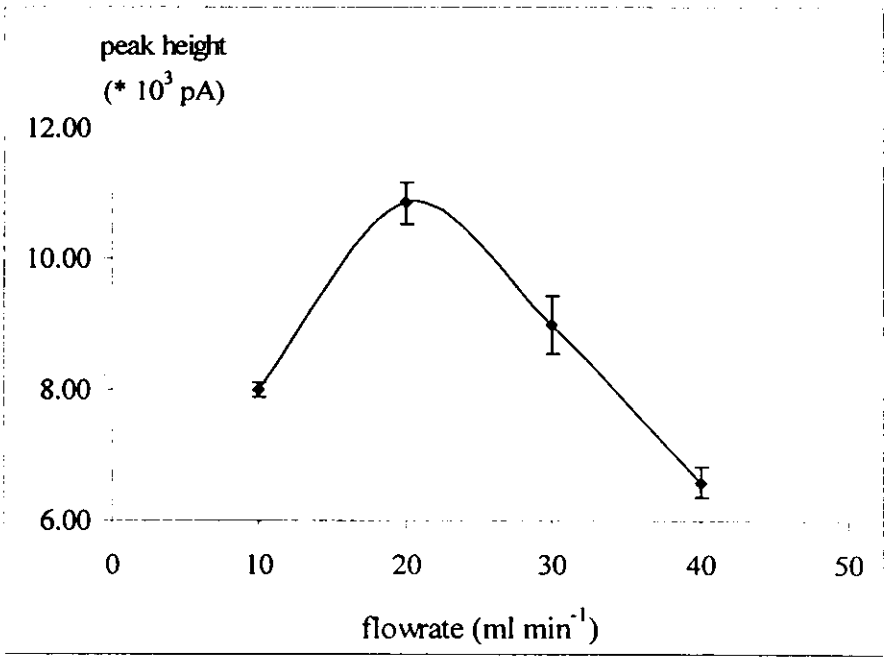
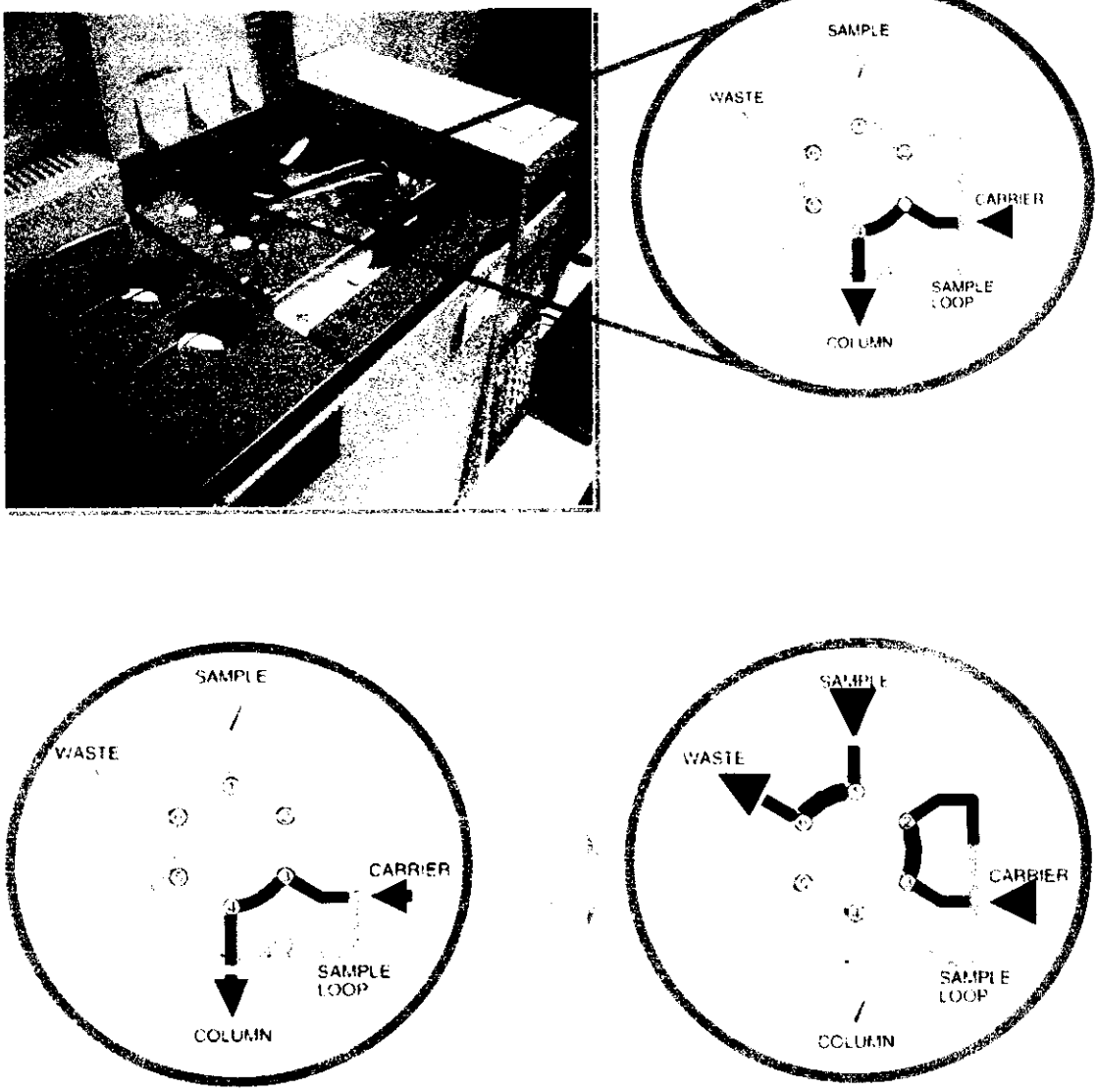


Figure 22 Response *versus* nitrogen flow rate of 0.25 mL, 0.34 μg mL^{-1} acetaldehyde standard gas

3.1.8 Valve heating time

The injector was modified to be used with a gas sampling valve as shown in Figure 23. Reproducibility with these valves is better than 0.5% (RSD) for a given loop (Grob, 1985). In the loading step, a known volume gas sample loop was filled, while the carrier gas was purge to the column directly to give a baseline. In the injection step, the valve was switched to the injection position where the sample in the loop is passed into the column to be separated and detected by flame ionization detector.

During the loading step, the valve was heated to prevent condensation of the less volatile components. The valve heating time is the time the sample was allowed to fill the sampling loop. The heating time was varied from 0.2 to 0.5 min the obtained results are shown in Table 9 and Figure 24. The highest response was at 0.3 minute, so the optimum valve heating time was 0.3 min.



Loaded

Injected

Figure 23 The gas sampling valve system

Table 9 Response of 0.25 mL, 0.34 μg mL^{-1} acetaldehyde standard gas at difference valve heating time

Time (min)	Response ($\times 10^3$)*, pA
0.2	11.58 ± 0.35
0.3	13.07 ± 0.20
0.4	11.55 ± 0.23
0.5	11.29 ± 0.42

* 4 replications, RSD < 4%

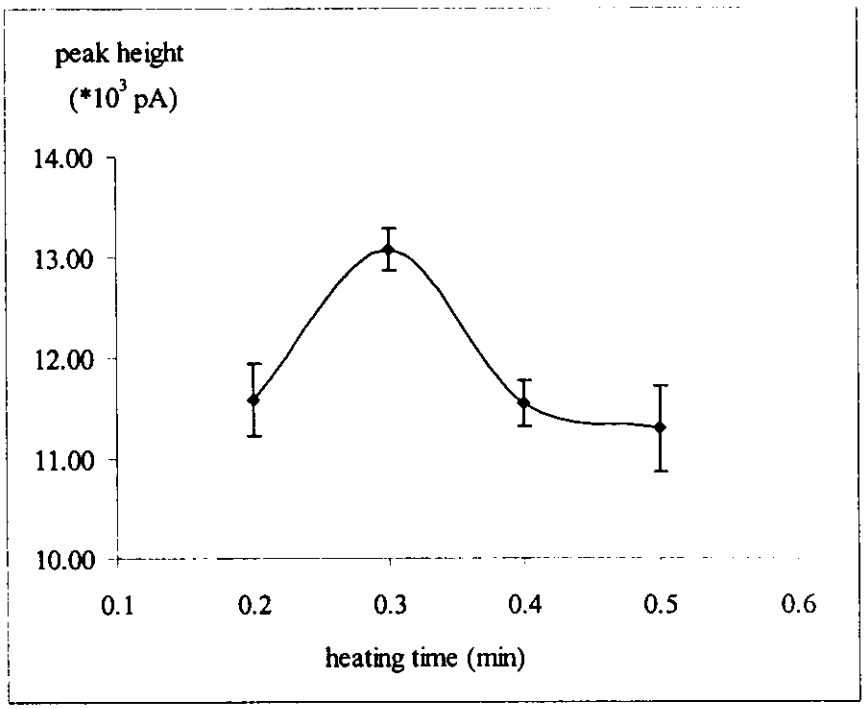


Figure 24 Response *versus* valve heating time of 0.34 μg mL^{-1}, 0.25 mL acetaldehyde standard gas

3.1.9 Summary of GC-FID conditions

The optimization of GC-FID conditions for acetaldehyde analysis could be summarized in Table 10 and the chromatogram of acetaldehyde is shown in Figure 25.

Table 10 The optimized conditions of GC-FID for acetaldehyde analysis

Condition	Optimized value
carrier gas flow rate	8.0 mL min^{-1}
column temperature	130 °C
detector temperature	270 °C
valve temperature	140 °C
fuel gas flow rate	30 mL min^{-1}
oxidant gas flow rate	300 mL min^{-1}
make up gas flow rate	20 mL min^{-1}
valve heating time	0.3 min

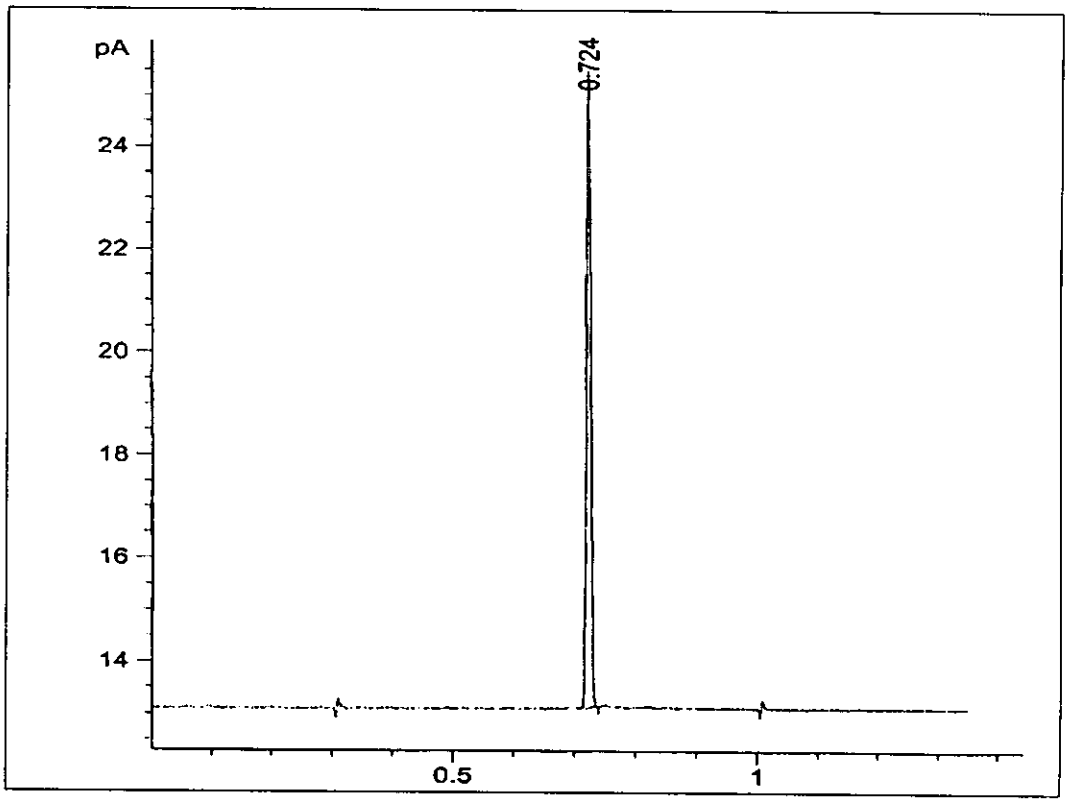


Figure 25 The chromatogram of acetaldehyde using the optimum conditions

3.2 Optimization of the airspace analysis conditions

Gas chromatographic technique is an analytical technique for investigating volatile organic compounds. Its sample is easily introduced into the analytical column if it is gas. However, if the sample is liquid or solid it must be transformed before the introduction.

The purpose of this work was to determine acetaldehyde that migrated from PET bottle. Thus a sample preparation technique was needed to transform acetaldehyde sample into gas phase. In this study, the airspace technique was used as the sample preparation technique. The equilibration temperature and time were the two main parameters influencing the airspace sensitivity. For acetaldehyde residue in PET bottles analysis, the conventional method was set at room temperature (22 °C ± 1.5 °C) as the equilibration temperature (Airspace acetaldehyde test, 1999). For

simplicity, the bottles were left to stand in room temperature at at 24 ± 2 °C. This was the equilibration temperature for the airspace condition.

3.2.1 Equilibration time

Equilibration time depended on the diffusion of the volatile components, acetaldehyde and other VOCs, from the sample. It was optimized in experiment 2.6.1. The results are shown in Table 11 and Figure 26. The response increased as the equilibration time increased from 1 to 2 minutes. Then the response decreased with time. After 20 minutes, the response was steady. This was the time acetaldehyde in the sample volatile into the gas phase and reached the equilibrium. However, the percentage of different of response between the time was less than 1 %, so the least time, 2 minutes, was selected to be the optimum equilibration time.

Table 11 Response of 0.25 mL, 0.34 μg mL^{-1} acetaldehyde standard gas at difference equilibration time

Equilibration time (min)	Response ($\times 10^3$)*, pA
1	7.22 ± 0.08
2	7.32 ± 0.04
3	7.28 ± 0.19
4	7.25 ± 0.13
5	7.08 ± 0.06
10	6.87 ± 0.14
20	7.10 ± 0.22
30	7.10 ± 0.19

* 4 replications, RSD < 4%

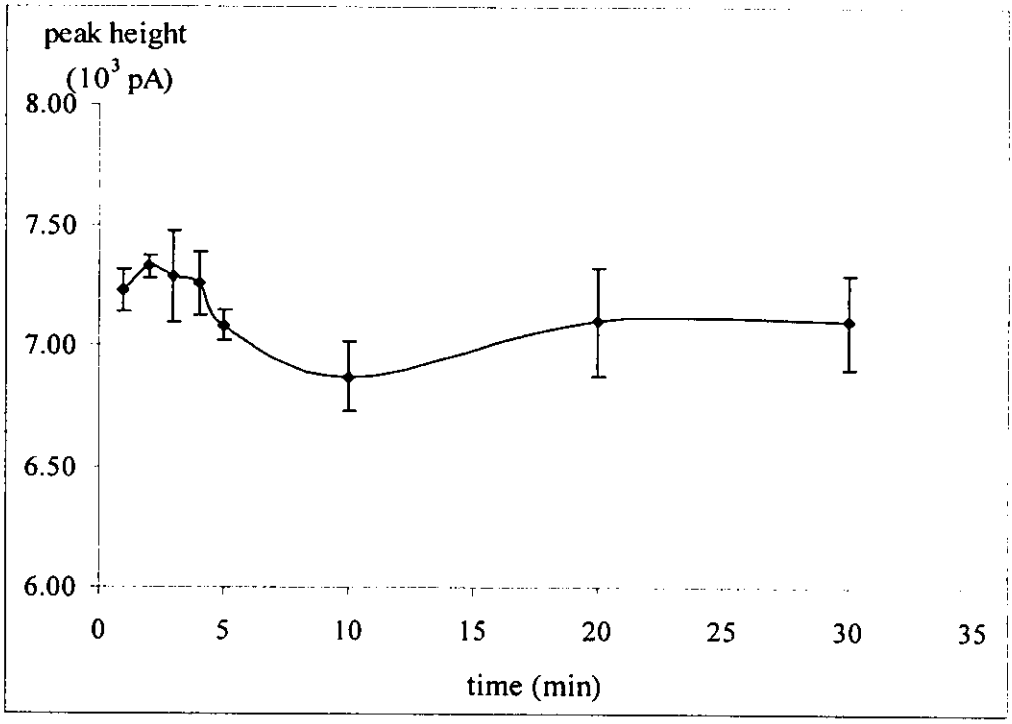


Figure 26 Response *versus* equilibration time of 0.25 mL, 0.34 μg mL^{-1} acetaldehyde standard gas

3.3 Linear dynamic range (LDR)

A linear dynamic range is the range of sample concentration over which the response factor based on area (height) measurement varies by less than plus or minus 20% (Grob, 1985). In practice, the linear dynamic range was demonstrated experimentally by running a series of concentrations as shown in Table 12 with relative standard deviation (RSD) less than 4 % for four replicates. These results were used to plot the calibration curve of acetaldehyde, as shown in Figure 27. The system showed a wide linear dynamic range, *i.e.*, 0.3 ng mL^{-1}- 6.6 μg mL^{-1} with a good correlation coefficient, $R^2 > 0.99$.

Table 12 Response at various concentrations of acetaldehyde

Concentration ($\mu g\ mL^{-1}$)	Response ($\times 10^3$)*, pA
0.002	0.046±0.003
0.003	0.096 ± 0.001
0.07	3.46 ± 0.06
0.13	4.22 ± 0.09
0.20	5.10 ± 0.16
0.27	6.08 ± 0.17
0.33	7.32 ± 0.18
1.67	24.39 ± 0.81
3.34	42.83 ± 0.84
6.68	75.80 ± 1.34

* 4 replications, RSD < 4%

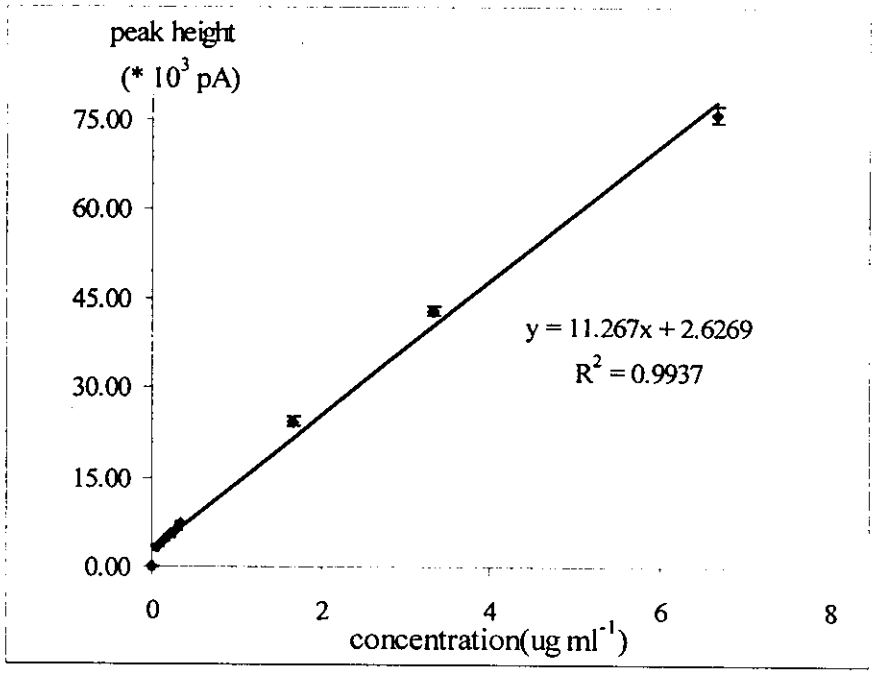


Figure 27 Response *versus* acetaldehyde concentrations

3.4 Limit of detection (LOD)

The method used for investigating limit detection was based on IUPAC method (Long and Winefordner, 1983) (2.7). First, a mean value of the blank response, $\bar{x}_B$, and the standard deviation were calculated using equation (1) and (2)

$$\bar{x}_B = \frac{\sum_{j=1}^{n_B} x_{Bj}}{n_B} \quad \ldots(1)$$

$$s_B^2 = \frac{\sum_{j=1}^{n_B} (x_{Bj} - \bar{x}_B)^2}{(n_B - 1)} \quad \ldots(2)$$

then , x_L was calculated by the equation

$$x_L = \bar{x}_B + ks_B \quad \ldots(3)$$

where k is a numerical factor chosen in accordance with the confidence level desired. c_L was then obtained as a function of x_L

$$c_L = \frac{(x_L - \bar{x}_B)}{m} \quad \ldots(4)$$

where m is the analytical sensitivity. Because the mean blank reading, $\bar{x}_B$, is not always 0, the signal must be background corrected. By substituting equation (3) into (4), equation (5) is obtained

$$c_L = \frac{ks_B}{m} \quad \ldots(5)$$

This definition of c_L can be illustrated as shown in Figure 28. The limit of detection is found by relating ks_B to a concentration value by dividing it with the slope of the calibration curve obtained from linear regression analysis.

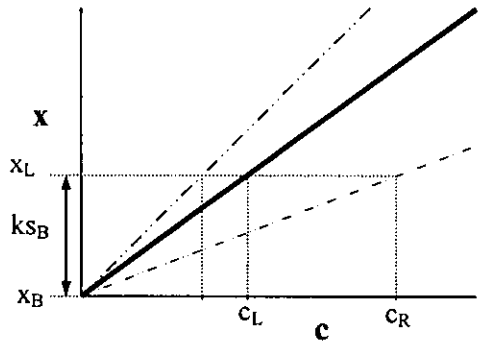


Figure 28 Analytical calibration curve of signal, x, *versus* concentration, c, showing the relationship between ks_B and the limit of detection, c_L (Long and Winefordner, 1983)

The data of blank measurements are shown in Table 13. These values were the maximum response of each running at various retention times, t_R. The smallest detectable signal, x_L, and standard deviation, s_B, were obtained by equation (1)-(3). x_L was 4.06 and s_B was 1.06. Using k = 3 together with the value of s_B and the slope of the calibration curves obtaining from Table 14 and Figure 29, the limit of detection for acetaldehyde, c_L, was 0.3 ng mL^{-1}.

Table 13 Data of the nitrogen blank measurements, $n_B = 20$

t_R	Maximum response, pA
0.311	5.20
0.723	1.50
0.723	1.60
0.723	1.40
0.723	0.77
0.723	0.53
0.723	0.75
0.723	0.52
0.723	0.52
0.723	0.47
0.723	0.43
0.722	0.37
0.722	0.58
0.722	0.42
0.310	0.40
0.310	0.42
0.310	0.42
0.310	0.44
0.310	0.41
0.310	0.42
	$\overline{x}_B = 0.88$
	$s_B^2 = 1.12$

Table 14 Response of acetaldehyde at various concentrations

Concentration (ng mL^{-1})	Response*, pA
0.37	1.50 ± 0.10
0.74	4.51 ± 0.48
1.04	7.91 ± 0.33
1.50	12.39 ± 0.56

* 4 replications, RSD < 4%

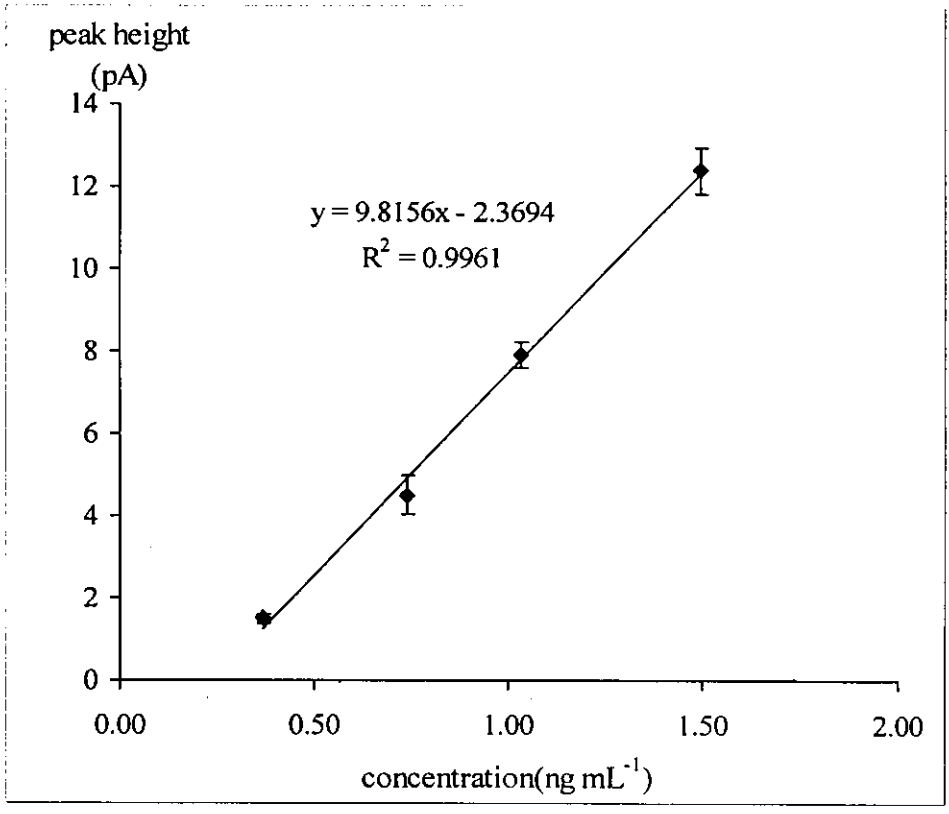


Figure 29 The calibration curve of acetaldehyde

3.5 Lab- built heating box

3.5.1 Temperature calibration of a lab-built heating box

The temperature of a lab-built heating box was calibrated using the modified lid I to obtain the correct temperature. The results are shown in Table 15 and Figure 30. For the modified lid II, the results are shown in Table 16 and Figure 31.

Table 15 Relationship between the set temperature and the actual temperature of the lab-built heating box obtained from the multimeter using modified lid I

(* in most cases all measurements provided the same results and standard deviation was 0, in this case we record the least count)

Set temperature (°C)	Correct temperature ± least count * (°C)
40	45 ± 1
45	50 ± 1
50	55 ± 1
55	60 ± 1
60	65 ± 1

* 5 replications, RSD < 4 %

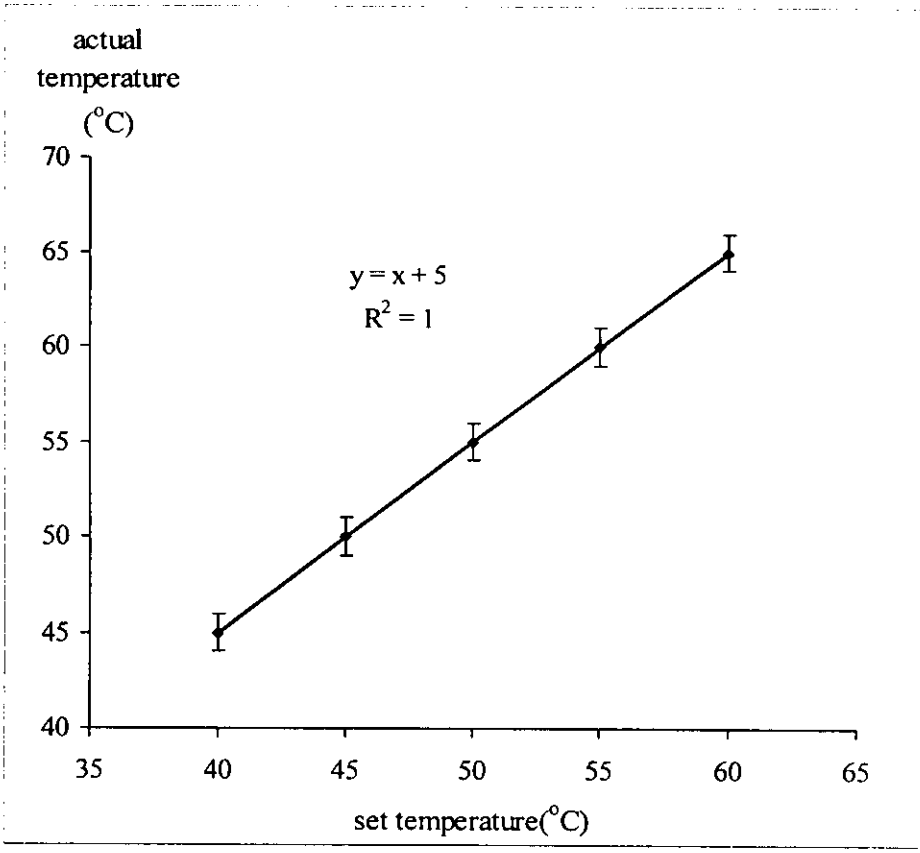


Figure 30 Actual temperature *versus* set temperature of lab- built heating box using modified lid I

Table 16 Relationship between the set temperature and the actual temperature of the lab-built heating box obtained from the multimeter using modified lid II

Set temperature (°C)	Actual temperature ± least count (°C)
40	44 ± 1
45	49 ± 1
50	54 ± 1
55	59 ± 1

* 5 replications, RSD < 4 %

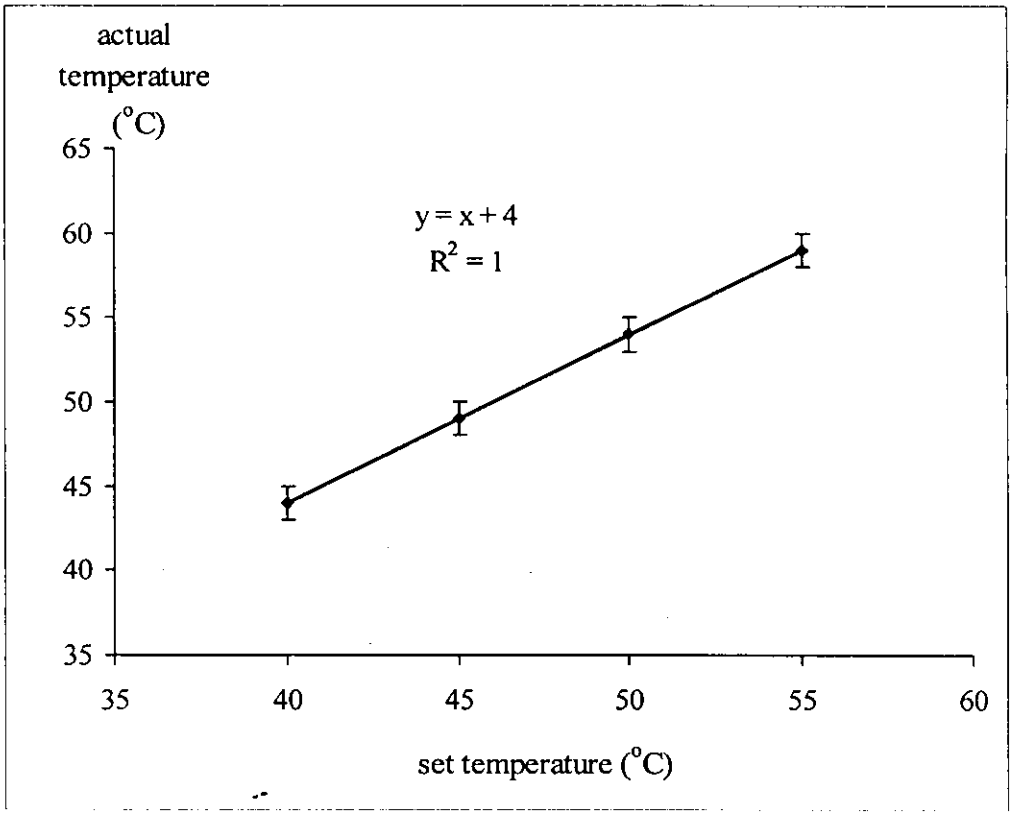


Figure 31 Actual temperature *versus* set temperature of lab- built heating box using modified lid II

3.5.2 Temperature of each position in the lab-built heating box

Five bottles were incubated in the heating box. The temperature of each position was compared to make sure that all bottles were incubated at the same temperature. The results are shown in Table 17 and Table 18 and were statistically compared by ANOVA. The null hypothesis adopted is that all the positions are the same temperature with mean μ and variance δ_0^2. On the basis of this hypothesis variance δ_0^2 can be estimated in two ways, one involving the variation within the positions and the other the variation between the positions. For each sample (*h* positions *n* members) a variance can be calculated by using the formula:

$$\text{Sample variance } (\delta_0^2) = \sum \frac{(X_i - \bar{X})^2}{(n-1)}$$

$$\text{Within- sample estimate of } \delta_0^2 = \sum_i \sum_j \frac{(X_{ij} - \bar{X}_i)^2}{h(n-1)}$$

$$\text{Between- sample estimate of } \delta_0^2 = n \sum_i \frac{(\bar{X}_i - \bar{X})^2}{(h-1)}$$

If the null hypothesis is correct, then these two estimates of δ_0^2 should not differ significantly. If it is incorrect, the between- sample estimate of δ_0^2 will be greater than the within- sample estimate because of between- sample variation. This experiment the analyst has no idea, prior to the experiment, as to whether any difference temperature between the positions will be positive or negative. Thus the test used must cover either possibility (Miller and Miller, 2000). Therefore, a two-sided F-test is used:

F = Between- sample estimate of δ_0^2/ Within- sample estimate of δ_0^2.

If the calculated value of F is greater than the critical value of F, the null hypothesis is rejected: the sample means do differ significantly (Miller and Miller, 2000).

Table 17 Temperature of the five positions in the lab- built heating box using modified lid I

Position	Temperature ± SD* (°C)
1	36.3 ± 0.6
2	36.0 ± 1.0
3	36.3 ± 0.6
4	35.3 ± 1.5
5	35.6 ± 0.6

* 3 replications, RSD < 4 %

From Table 17, ANOVA test was used to compare the temperature of the five positions.

For each position (5 positions 3 replicates) a variance can be calculated by using the above formula. The mean of each position were 36.3, 36.0, 36.3, 35.3, and 35.6, respectively. Variance of sample 1, 2, 3, 4 and 5 were 0.34, 1.00, 0.34, 2.34 and 0.34, respectively. Within- sample estimate of δ_0^2 were 0.87. For between- sample estimate of δ_0^2 was 1.31.

The calculated F value was 1.51, compared this with the F critical value of h = 5, n = 3 of 4.47 ($P < 0.05$), the calculated value was lower than the value from the table. Thus, the null hypothesis was retained, that is, there were no significant difference temperature among five positions.

Table 18 Temperature of the five positions in the lab- built heating box using a modified lid II

Position	Correct temperature from multimeter ± least count* (°C)
1	59 ± 1
2	59 ± 1
3	59 ± 1
4	59 ± 1
5	59 ± 1

* 5 replications, RSD < 4 %

After the preliminary study, the modified lid II was designed and calibrated as the modified lid I. From Table 18, the temperature of all positions is exactly the same. Thus, five bottles hang at five positions were incubated at the same temperature in lab- built heating box using the modified lid II.

3.6 Optimum conditions of the developed technique

3.6.1 Incubation temperature

The effect of incubation temperature on the release of acetaldehyde (response) is shown in Table 19 and Figure 32. When the temperature increased, the response increased because higher temperature helped to release acetaldehyde. The optimized temperature was the temperature that gave the highest response. Thus 60 °C (the maximum incubation temperature before the bottle changed shape) was chosen as the optimum temperature.

Table 19 Response of acetaldehyde at various incubation temperatures

Temperature (°C)	Response ± SD *, pA
37	0.17 ± 0.00
42	0.31 ± 0.02
50	0.46 ± 0.03
60	1.04 ± 0.04

* 5 replications, RSD < 10%

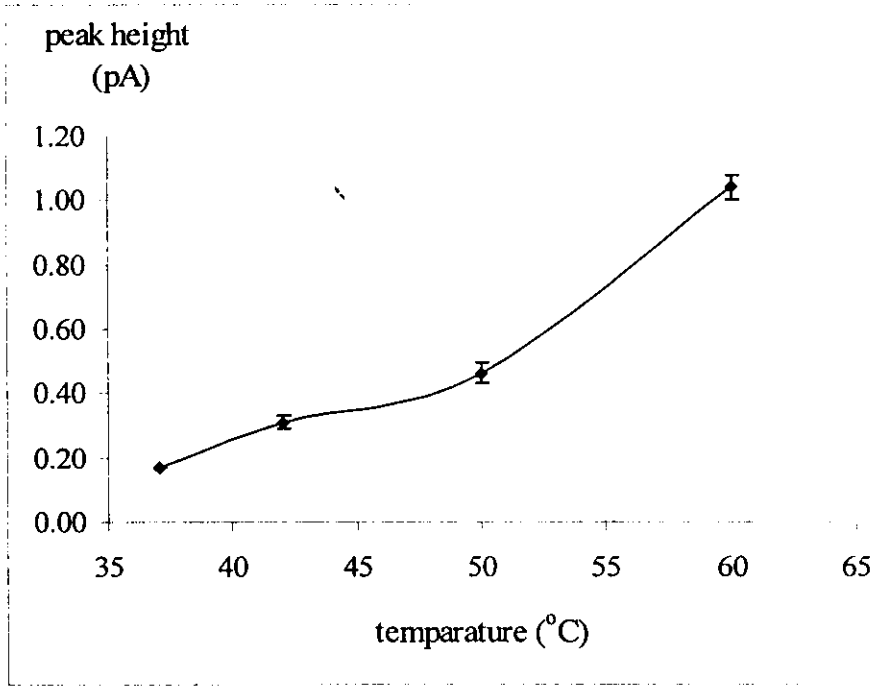


Figure 32 Response *versus* incubation temperature

3.6.2 Incubation time

Five newly blown 1.25 L PET bottles were incubated at 60 °C (the optimum incubating temperature) for 1, 3, 5, 7, and 9 hours. Gas sample in the bottles was then analyzed by gas chromatographic with flame ionization detector (GC-FID) at optimum conditions. The resulted peak heights are shown in Table 20 and Figure 33.

The longer the incubation time, the higher the response, that is, more acetaldehyde was released from the bottle. The optimum time was taken as the minimum time that gave the same or better response as conventional method (1.02 ± 0.08). Thus, an hour was chosen as the optimum incubating time.

Table 20 Response of acetaldehyde at various incubation times

Time (hr)	Response ± SD *, pA
1	1.04 ± 0.04
3	1.91 ± 0.10
5	2.36 ± 0.10
7	2.81 ± 0.06
9	3.11 ± 0.16

* 5 replications, RSD < 10%

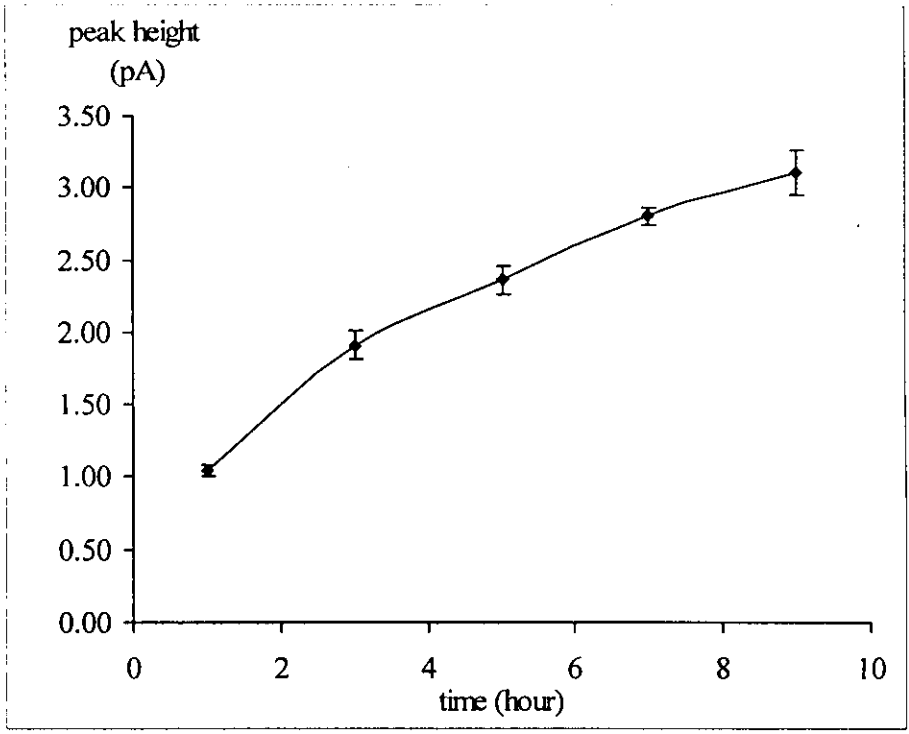


Figure 33 Response of acetaldehyde *versus* incubation time

3.7 Purge and trap technique

In order to handle the sample more easily and also to preconcentrate the gas sample, purge and trap technique was used. Acetaldehyde that migrated into PET bottle was adsorbed on adsorbent, followed by thermal desorption to gas chromatography analysis. Porapak Q, because of its property, was chosen to be the adsorbent.

3.7.1 Adsorbent conditioning

Porapak Q, 80/100 mesh was conditioned in the laboratory-built apparatus (experiment 2.12.1) by purging nitrogen through the adsorbent under heat at 200 °C for 3 hours. During this time, the round-bottom flask container was gently shaken occasionally to prevent the temperature gradient. The chromatogram obtained by the treated Porapak Q after conditioned (Figure 34) showed that this temperature (200 °C)

was high enough to remove contamination that could disturb the acetaldehyde desorption process.

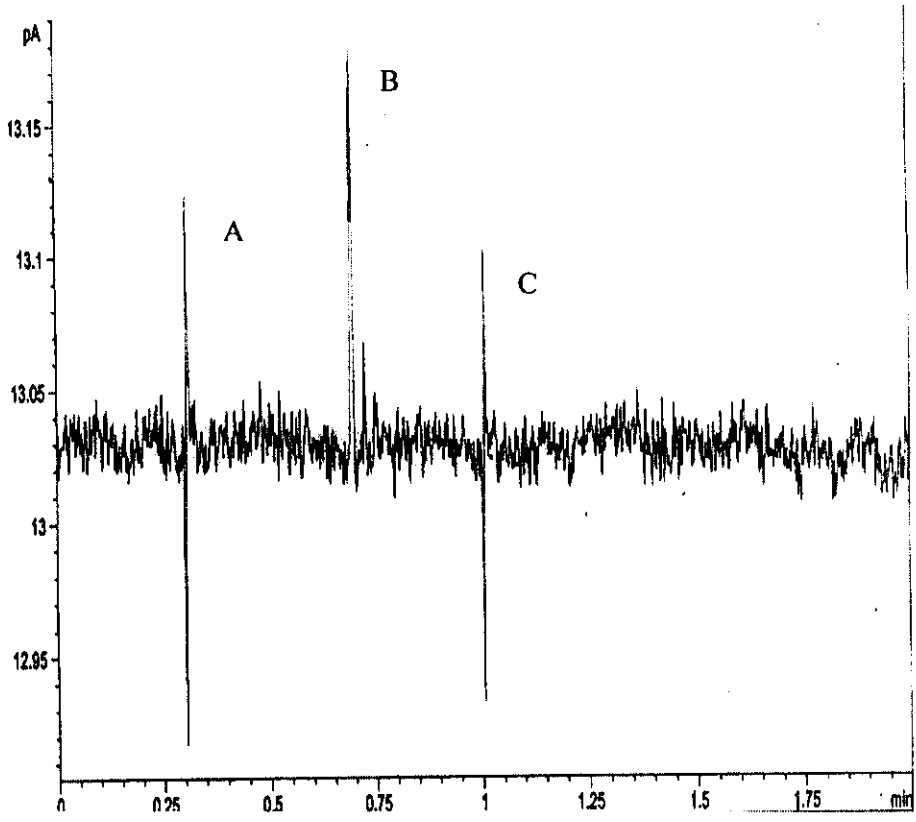


Figure 34 Chromatogram of the conditioned Porapak Q: A and C: Peak obtained when valve was switching; B: Small contaminant peak

3.7.2 Adsorbent tube preparation

The adsorbent tube was prepared as described in 2.12.2. After packing, the adsorbent tube was immediately sealed with a plastic end cap and kept in the desiccator to prevent air from diffusing into the tube during storage.

3.8 Optimization of adsorption conditions

3.8.1 Amount of adsorbent

The amount of adsorbent depended on the amount of acetaldehyde that migrated from PET bottles. If it was too low, some analyte might be lost. Using the adsorbent tube for sampling, the limit of the analyte from the bottle that could be concentrated without the sampling being lost (called "sampling capacity") must be evaluated (2.12.3). The results Table 21, Figure 35 showed that the response increased with the amount of adsorbent until 80 ± 5 mg, when the response became constant. The optimum amount of adsorbent was chosen as 80 mg.

Table 21 Response of acetaldehyde using various amounts of adsorbent

Amount of adsorbent (mg)	Response ± SD *, pA
40	62.5 ± 5.9
60	153.2 ± 8.0
80	191.5 ± 2.7
100	184.7 ± 13.6

* 5 replications, RSD < 10%

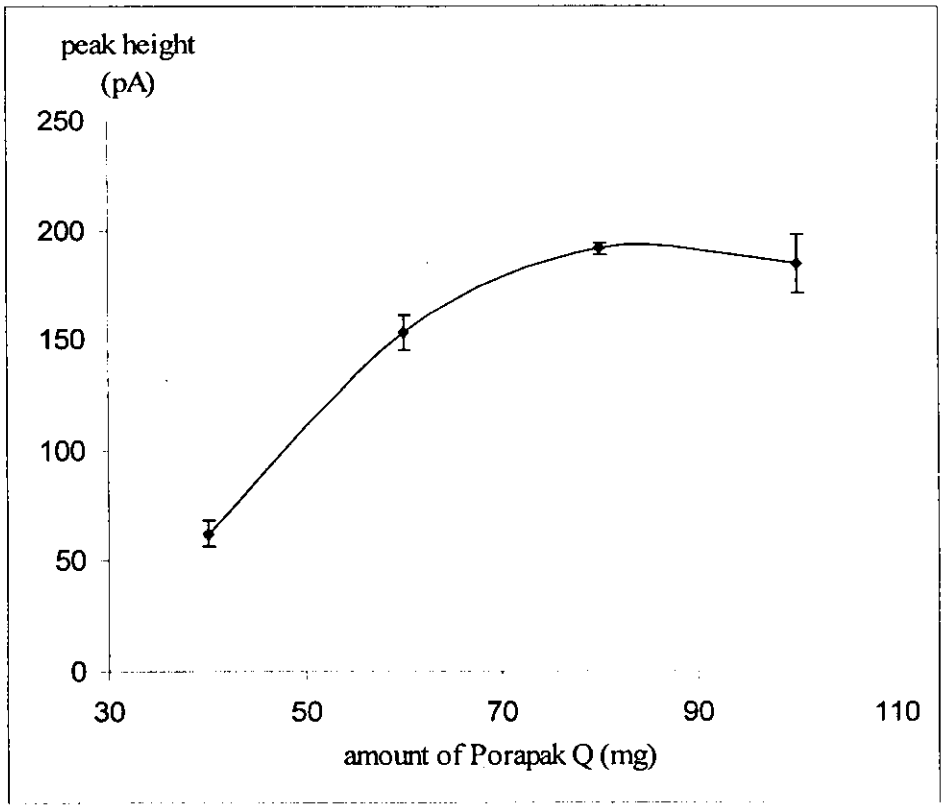


Figure 35 Response *versus* amount of adsorbent (Porapak Q)

3.8.2 Adsorption flow rate

Adsorption flow rate was an important parameter in a sampling process, since it would affect the adsorption efficiency of the adsorbent. Acetaldehyde was drawn through the adsorbent tube with different flow rate and its influence on the response is shown in Table 21 and Figure 36.

From 60 to 70 mL min^{-1}, the response increased when the flow rate increased because at fixed adsorption time, more flow rate, more volume of gas passed through the bottle, that is, more acetaldehyde was carried to adsorb on the adsorbent. At higher flow rate the response decreased. This is because at higher adsorption flow rate, the back pressure increased while the retain time of in acetaldehyde the adsorbent tube decreased and these reduced the adsorption efficiency. From the results, the optimum adsorption flow rate which gave the highest response was at 70 mL min^{-1}.

Table 22 Response of acetaldehyde at various adsorption flow rates

Adsorption flow rate (mL min $^{-1}$)	Response ± SD *, pA
60	11.0 ± 0.9
70	20.0 ± 1.9
80	13.3 ± 0.7
90	12.0 ± 1.0
100	5.5 ± 0.4

* 5 replications, RSD < 10%

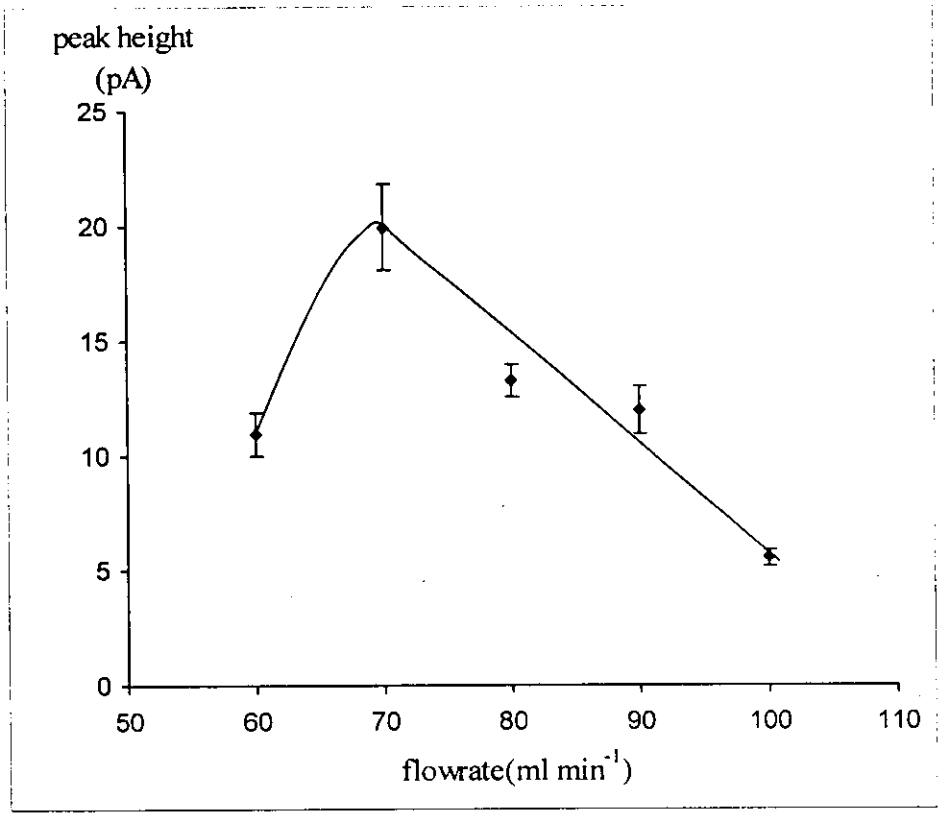


Figure 36 Response of acetaldehyde *versus* adsorption flow rate

3.8.3 Adsorption time

The adsorption time was the appropriate time for acetaldehyde to be completely adsorbed on the adsorbent in the adsorbent tube. The relationship between the adsorption time and the response is illustrated in Table 23 and Figure 37. The response increased with time from 10 to 15 minutes and leveled off. That is, all acetaldehyde were adsorbed on the adsorbent after 15 minutes.

Table 23 Response of acetaldehyde at various adsorption times

Adsorption time (min)	Response ± SD *, pA
10	12.2 ± 0.9
15	20.0 ± 1.9
20	19.5 ± 1.7
25	19.7 ± 1.9

* 5 replications, RSD < 10%

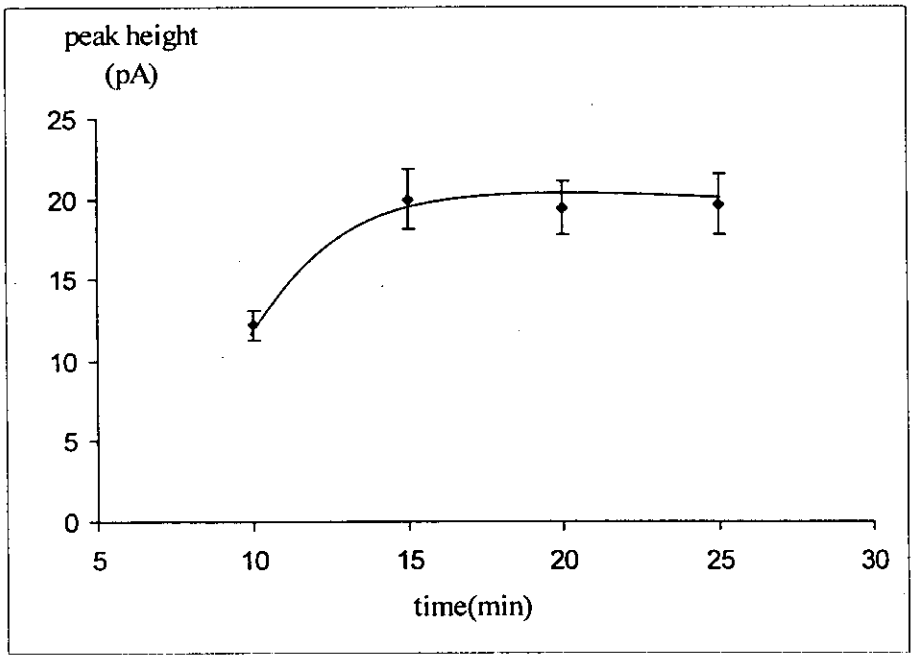


Figure 37 Response of acetaldehyde *versus* adsorption time

3.8.4 Storage lifetime of the adsorbent tube

The storage lifetime of the adsorbent tube was investigated to find out how long the adsorbed analyte could be kept before being analyzed. This was done by comparing the response of the adsorbed samples at 3 days intervals. Table 24 and Figure 38 show the effect of the storage time to the response of acetaldehyde when the tubes were stored at ambient temperature and in the refrigerator. Acetaldehyde responses were closed to the same level of the adsorbent tubes that were kept at room temperature for 12 days and 6 days, respectively. This indicated that temperature had some affect on the stability of the adsorbed acetaldehyde after 6 days. This indicated that the acetaldehyde adsorbed on the Porapak Q, 80/100 mesh was relatively stable and can be analyzed within 6 and 12 days when kept at room temperature and refrigerator storage, respectively.

Table 24 Response of acetaldehyde adsorbed on Porapak Q, 80/100 mesh adsorbent tube store at room temperature and in the refrigerator at various storage times

Storage time (day)	Response ± SD *, pA	
	Room temperature	Refrigerator
0	241.4 ± 12.3	-
3	258.9 ± 24.6	254.2 ± 13.4
6	257.7 ± 31.7	235.2 ± 8.5
9	149.7 ± 6.4	242.0 ± 8.4
12	155.7 ± 14.1	244.7 ± 40.3
15	89.7 ± 7.3	218.7 ± 20.6

* 4 replications, RSD < 10%

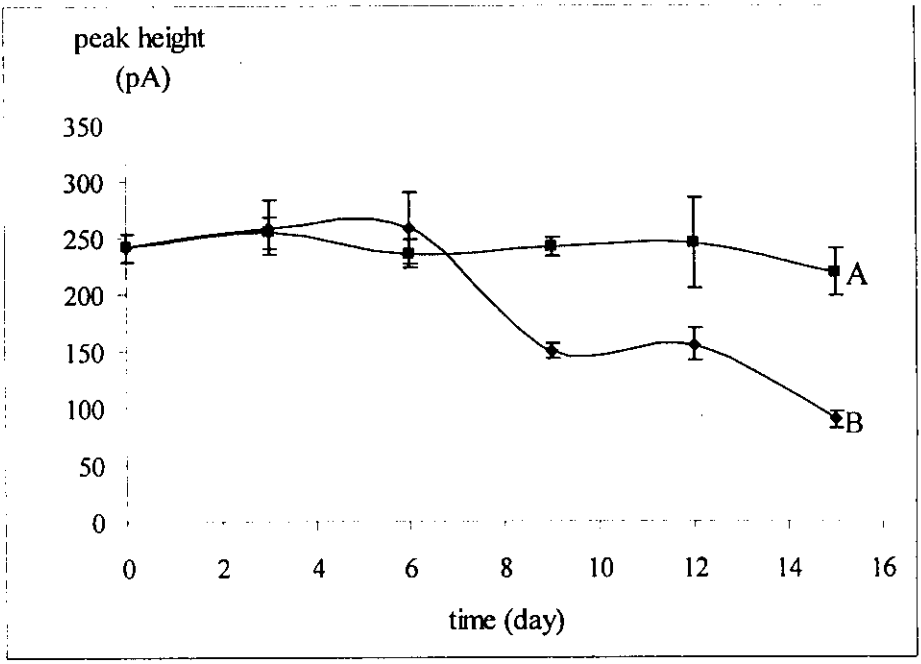


Figure 38 Response to acetaldehyde adsorbed on the adsorbent at different storage time A: refrigerator; B: room temperature

3.9 Lab-built thermal desorption unit

A lab-built thermal desorption unit was designed to thermally desorp the trapped acetaldehyde without the removal of adsorbent from the tube.

3.9.1 Temperature calibration

Prior to analysis, the temperature of the lab-built thermal desorption unit was calibrated to obtain the actual temperature and the results are shown in Table 25 and Figure 39. These were used for the rest of the experiments.

Table 25 The relationship between the set temperature and the actual temperature of the lab-built thermal desorption unit

Set temperature at temperature control unit (°C)	Actual temperature from multimeter ± SD*, (°C)
100	135 ± 1
150	198 ± 4
160	215 ± 4
170	225 ± 2
180	235 ± 1
200	260 ± 2

* 5 replications, RSD < 4 %

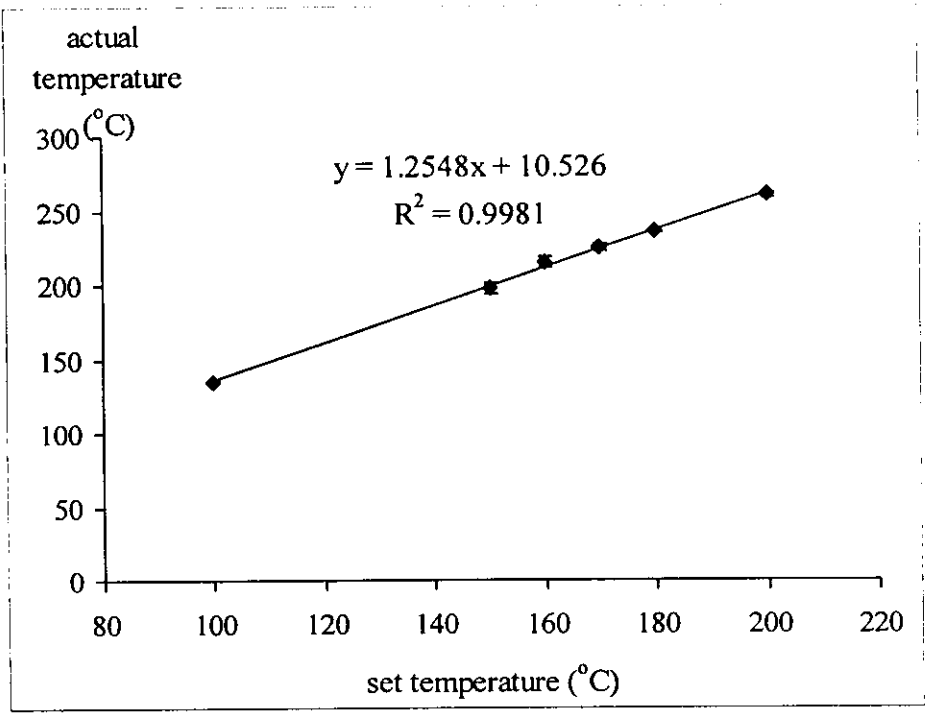


Figure 39 Calibration curve showing the relationship between the set and actual temperature of thermal desorption unit

3.10 Optimization of the desorption conditions

For thermal desorption, to reduce error and complication from adsorption process direct injection was used. Several parameters must be optimized, *i.e.*, desorption temperature, desorption flow rate and desorption time.

3.10.1 Desorption flow rate

The effect of desorption flow rate on the elution of acetaldehyde was evaluated. The results are shown in Table 26 and Figure 40 and it could be observed that the desorption process occurred rapidly between 60 and 70 mL min^{-1}. This was because at a fixed desorption time, the higher the flow rate, the more amount of acetaldehyde could be carried to the column. After 70 mL min^{-1} the response decreased. This was probably caused by the back pressure. Thus, the optimum desorption flow rate was 70 mL min^{-1}.

Table 26 Response of acetaldehyde at various desorption flow rate

Desorption flow rate (mL min^{-1})	Response ± SD *, pA
60	18.6 ± 0.9
70	35.4 ± 2.0
80	23.9 ± 1.2
90	24.4 ± 1.3
100	30.7 ± 1.4

* 5 replications, RSD < 10%

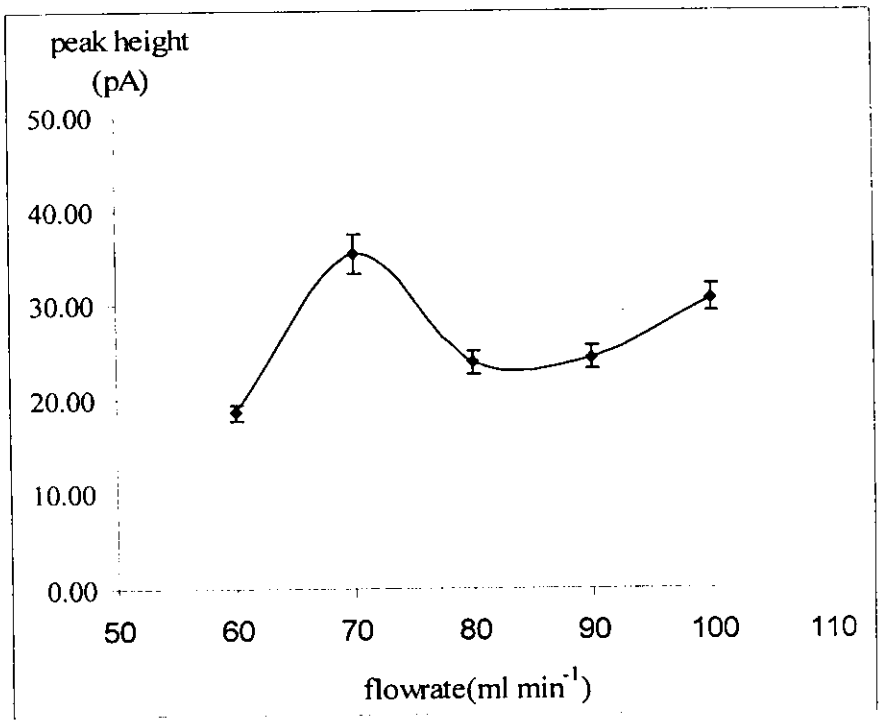


Figure 40 Response of acetaldehyde *versus* desorption flow rate

3.10.2 Desorption time

The optimum desorption time was investigated and the results are shown in Table 27 and Figure 41. The response increased with time up to 0.6 min then became constant. This indicated that the complete desorption process occurred at 0.6 min. Therefore the optimum desorption time was 0.6 min.

Table 27 Response of acetaldehyde at various desorption times

Desorption time (min)	Response ± SD*, pA
0.3	35.4 ± 2.1
0.4	67.4 ± 3.0
0.5	101.8 ± 7.9
0.6	142.7 ± 4.9
0.7	129.3 ± 3.6
0.8	134.8 ± 7.3

* 5 replications, RSD < 10%

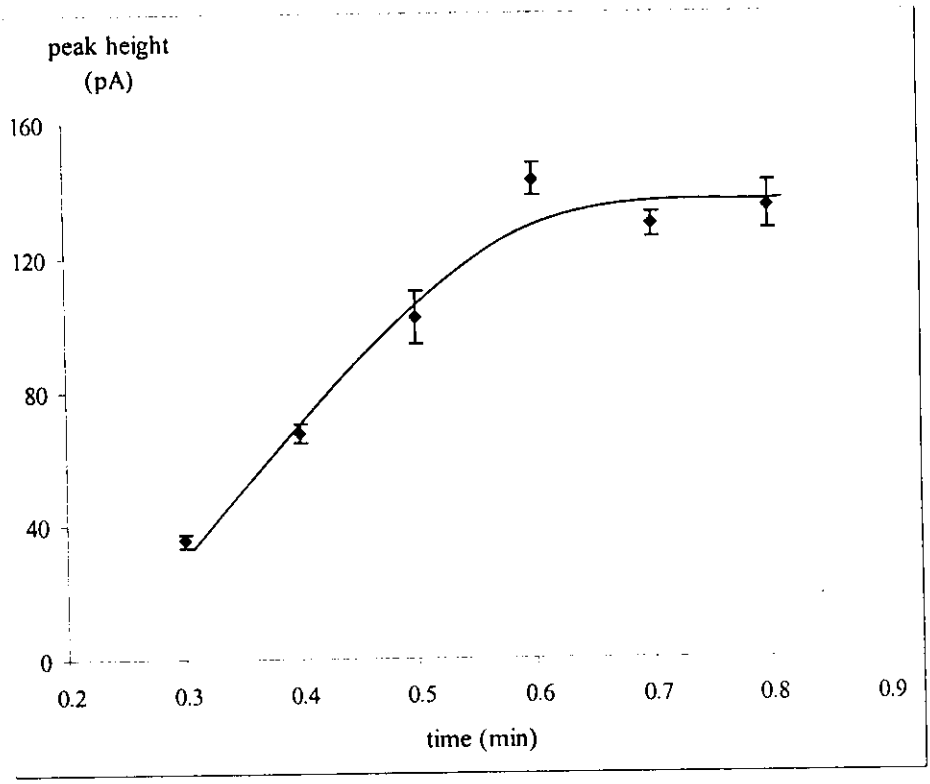


Figure 41 Response of acetaldehyde *versus* desorption time

3.10.3 Desorption temperature

In this study, the desorption temperature was tested between 198 and 245 °C. The lower value was from our preliminary study and this was higher than the boiling point of acetaldehyde. This was to ensure that acetaldehyde could be completely eluted from the trap. For the upper limit, 245 °C, the maximum temperature of adsorbent should also be considered in order to prevent the damage of adsorbent and to increase its lifetime. Since Porapak Q was a porous polymer resin based on polydivinylbenzene, heating at high temperature would affect the chemical bonding of the polymer. The maximum temperature of Porapak Q is 250 °C (Alltech Chromatography Sourcebook, 2004), thus, the maximum desorption temperature was tested at 245 °C.

The effect of desorption temperature on the desorption (response) of acetaldehyde is shown in Table 28 and Figure 42.

The optimum temperature was considered from the minimum temperature which achieved the highest response. The results indicated that a low desorption temperature would provide an incomplete desorption of acetaldehyde. The highest response was obtained at 215 °C, and this was chosen as the optimum desorption temperature. After 215 °C, the response decreased, this might be because the temperature was near to the maximum temperature of adsorbent and this might affect the desorption efficiency.

Table 28 Response of acetaldehyde at various desorption temperatures

Desorption temperature (°C)	Response ± SD *, pA
198	94.0 ± 3.2
215	142.7 ± 4.9
225	98.3 ± 8.1
235	127.9 ± 9.9
245	125.6 ± 8.6

*5 replications, RSD < 10%

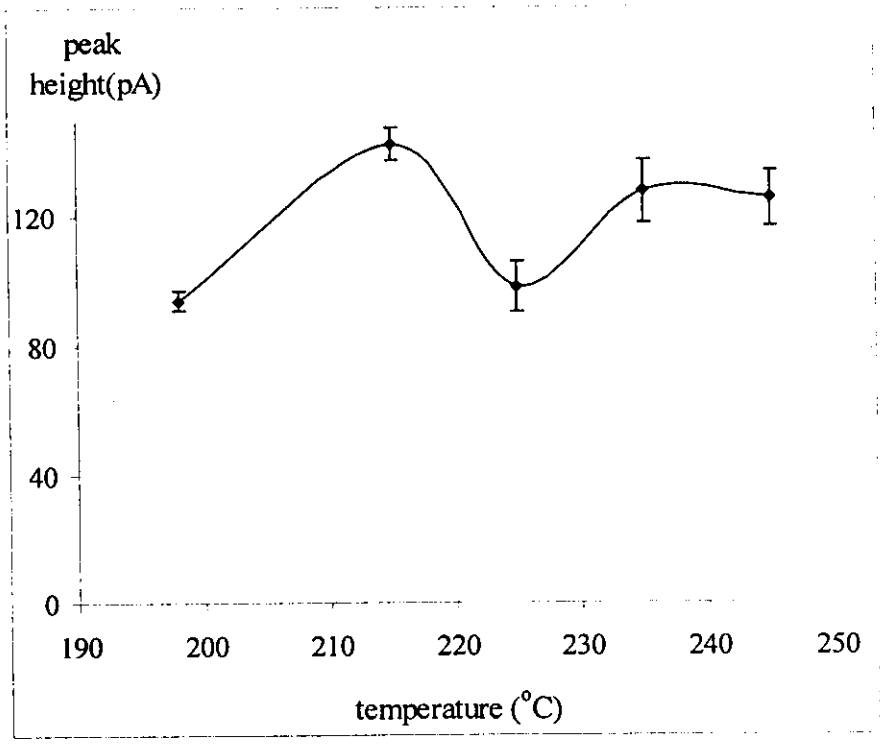


Figure 42 Response of acetaldehyde *versus* desorption temperature

3.11 Calibration curve of acetaldehyde

Standard acetaldehyde gas spiked into the PET bottles was collected in the adsorbent tube by active sampling. The adsorbent was then desorbed and acetaldehyde was analyzed. A calibration curve was obtained by plotting the subtracted blank (a 0 mL spiking) responses (peak height) *versus* the acetaldehyde content. The results are shown in Table 29 and Figure 43.

Table 29 Response of acetaldehyde at various concentrations (ng mL^{-1})

Amount of acetaldehyde (ng mL^{-1})	Response ± SD *, pA
0.26	0.92 ± 0.02
0.52	3.67 ± 0.23
0.74	6.32 ± 0.06
1.05	10.95 ± 0.06

* 5 replications, RSD < 10%

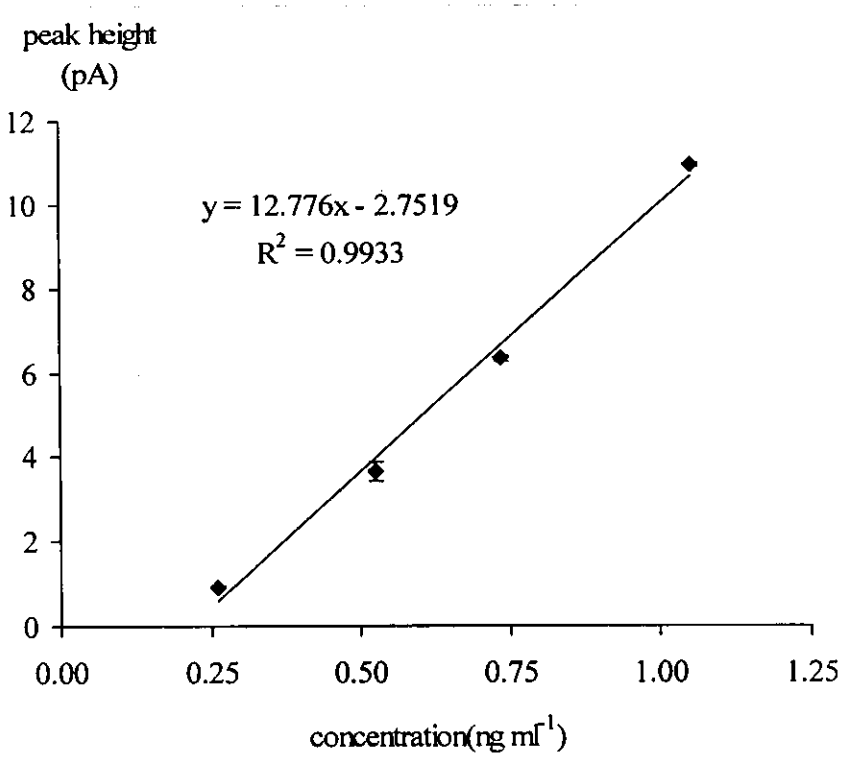


Figure 43 Calibration curve of acetaldehyde

3.12 Qualitative and quantitative analysis of acetaldehyde residue in PET bottles

For real sample anaysis, newly blown bottle samples were collected from Haad Thip Co. Ltd., Hat-Yai, Songkhla. There are three types of PET bottle (Figure 44), Coke, Sprite, and Fanta, 1.25 and 2 l (Figure 45). A total of 1160 PET bottles were analyzed at optimum conditions between September, 2003 and August, 2004. The chromatogram of acetaldehyde from real sample analysis is shown in Figure 46.

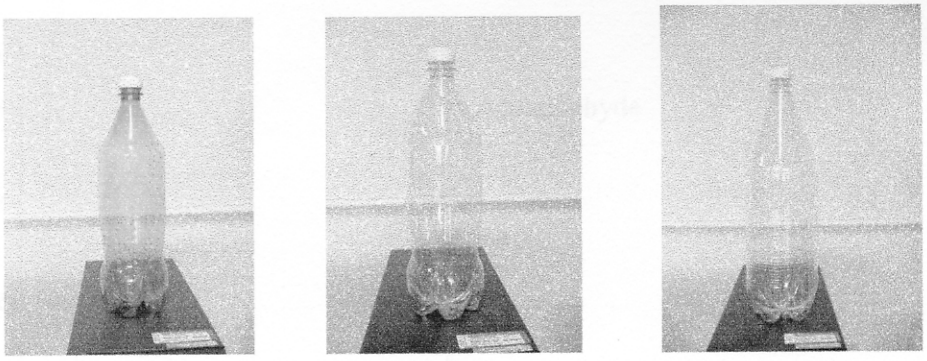


Figure 44 Newly blown PET bottles from Haad Thip Co., Ltd.

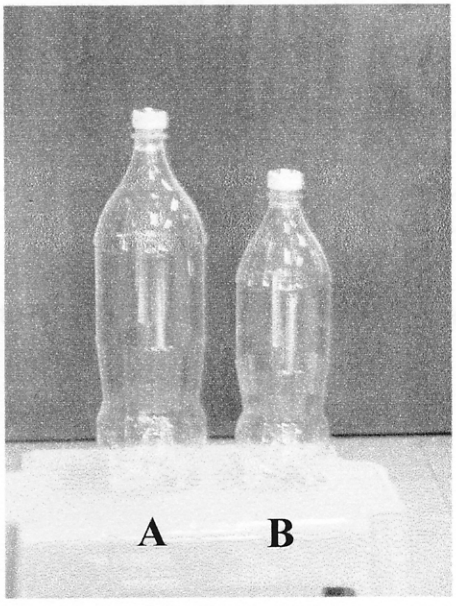


Figure 45 Newly blown Coke bottle A = 2 L; B = 1.25 L

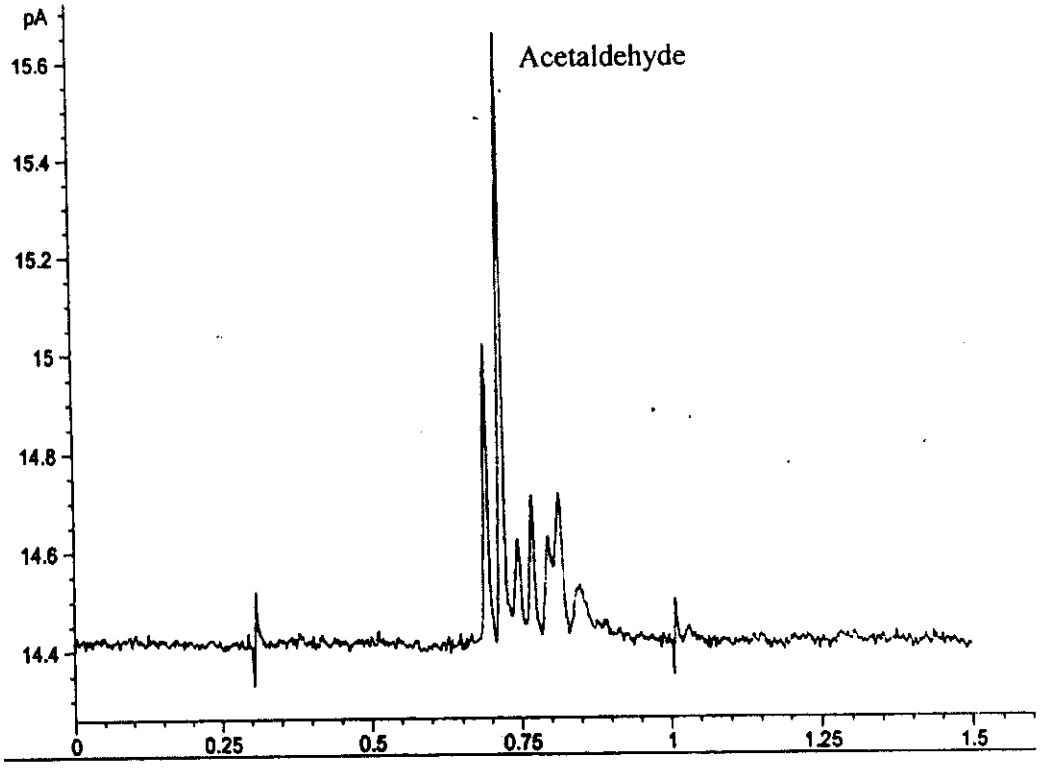


Figure 46 The acetaldehyde chromatogram from real sample analysis

3.12.1 Comparison between conventional and proposed methods

The sampling of PET bottles depends on the company production. For each sampling, 60 PET bottles were collected, 45 to be analyzed by the proposed method and 15 by the conventional method. The results of the two methods were compared using *t*- test. In this test the two sample means $\bar{X}_1$ (conventional method) and $\bar{X}_2$ (proposed method) was compared. The null hypothesis was that both methods gave the same result and to test whether $(\bar{X}_1 - \bar{X}_2)$ differed significantly from zero. If the two samples had standard deviations which were not significantly different, a pooled estimate, of the standard deviation can be calculated from the two individual standard deviations s_1 and s_2, and the statistic *t* is calculated by

$$t = \frac{(\bar{X}_1 - \bar{X}_2)}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

Where s is calculated from

$$s^2 = \frac{(n_1 - 1)s_1^{\,2} + (n_2 - 1)s_2^{\,2}}{(n_1 + n_2 - 2)}$$

and *t* has n_1+n_2 - 2 degree of freedom.

The results from conventional and proposed method are shown in Table 30.

Table 30 Comparison between acetaldehyde concentrations obtained from conventional and proposed methods

- Method 1 : Conventional method; n_1 : the number of bottle for method 1; $\bar{X}_1$: the mean of method 1 results; s_1 : the standard deviation of method 1 results
- Method 2 : Proposed method n_2 : the number of bottle for method 2; $\bar{X}_2$: the mean of method 2 results; s_2 : the standard deviation of method 2 results

Type	Size (L)	Date	Resin/ Supplier	Blowing Temp. (°C)	Method1 (ng mL^{-1})	Method2 (ng mL^{-1})	n_1	n_2	$\bar{X}_1$	$\bar{X}_2$	s_1	s_2	t
Coke	1.25	24/09/03	5015X/The PET	210	0.35-0.39	0.36-0.42	15	45	0.37	0.39	0.02	0.03	2.22
Fanta	1.25	30/09/03	Indo PET/PET Asia	210	0.46-0.52	0.47-0.55	15	45	0.49	0.51	0.03	0.04	1.67
Sprite	1.25	29/09/03	5015X/PET Pack	240	0.33-0.37	0.35-0.39	10	45	0.35	0.37	0.02	0.02	2.70
Coke	1.25	08/10/03	Indo PET/PET Asia	210	0.47-0.57	0.45-0.55	15	45	0.52	0.50	0.05	0.05	1.33
Sprite	1.25	29/10/03	Indo PET/PET Asia	210	0.52-0.62	0.53-0.63	15	45	0.57	0.58	0.05	0.05	0.53
Fanta	2	06/01/04	5015X/PET Pack	240	0.41-0.42	0.39-0.47	10	20	0.41	0.43	0.01	0.04	1.51
Sprite	2	06/01/04	5015X/PET Pack	210	0.39-0.41	0.39-0.47	10	20	0.40	0.43	0.01	0.04	2.56
Sprite	1.25	19/01/04	Indo PET/PET Asia	210	0.45-0.59	0.48-0.58	10	20	0.52	0.53	0.07	0.05	0.43

Table 30 (continued)

Type	Size (L)	Date	Resin/Supplier	Blowing Temp. (°C)	Method1 (ng mL^{-1})	Method2 (ng mL^{-1})	n_1	n_2	$\bar{X}_1$	$\bar{X}_2$	s_1	s_2	t
Fanta	1.25	19/01/04	Viridian/ Kianjoo	210	0.50-0.67	0.57-0.69	10	20	0.59	0.63	0.08	0.06	1.83
Fanta	1.25	17/05/04	Viridian/ Kianjoo	210	0.66-0.76	0.71-0.79	15	45	0.71	0.75	0.05	0.04	2.66
Fanta	1.25	18/05/04	Viridian/ Kianjoo	210	0.80-0.96	0.77-0.95	15	45	0.88	0.86	0.08	0.09	0.74
Fanta	1.25	21/05/04	Viridian/ Kianjoo	210	0.70-0.82	0.69-0.83	15	45	0.76	0.76	0.06	0.07	0.19
Coke	1.25	22/05/04	CB-608/ PET Far	210	1.01-1.13	0.98^{-1}.20	15	45	1.07	1.09	0.06	0.11	0.66
Sprite	1.25	31/05/04	CB-608/ The PET	210	0.51-0.63	0.61-0.75	15	45	0.57	0.68	0.06	0.07	4.56
Sprite	2	28/05/04	Thai PET/ PET Pack	240	0.48-0.58	0.49-0.55	10	45	0.53	0.52	0.05	0.03	2.50
Coke	2	28/05/04	Thai PET/ PET Pack	240	0.61-0.71	0.56-0.72	10	20	0.66	0.64	0.05	0.08	0.83
Fanta	2	10/06/04	Thai PET/ PET Pack	240	0.62-0.76	0.65-0.75	15	45	0.69	0.70	0.07	0.05	0.83
Fanta	2	21/06/04	5015X/ PET Pack	240	0.53-0.63	0.49-0.61	15	45	0.58	0.55	0.05	0.06	1.67
Coke	1.25	19/07/04	CB-608/ PET Far	210	0.48-0.52	0.49-0.55	15	45	0.50	0.52	0.02	0.03	2.22
Fanta	1.25	13/07/04	CB-608/ PET Far	210	0.55-0.57	0.51-0.59	15	45	0.56	0.55	0.01	0.04	1.23
Sprite	1.25	22/07/04	CB-608/ PET Far	210	0.43-0.45	0.41-0.47	15	45	0.44	0.44	0.01	0.03	0.56
Coke	1.25	04/08/04	CB-608/ PET Far	210	0.50-0.54	0.51-0.57	15	45	0.52	0.54	0.02	0.03	2.22

Table 31 Comparison the results (acetaldehyde concentration) between the proposed method and purge and trap technique

- Method 1 : Proposed method; n_1 : the number of bottle for method 1; Rank $_1$: the rank sum of method 1 results; U_1 : the U value of method 1 results; U_{crit} : Critical U value from U-table
- Method 2 : Purge and trap method n_2 : the number of bottle for method 2; Rank $_2$: the rank sum of method 2 results; U_2 : the U value of method 2 results

Type	Date	method1 ($ng\ mL^{-1}$)	method2 ($ng\ mL^{-1}$)	n_1	n_2	$Rank_1$	$Rank_2$	U_1	U_2	U_{crit} ($P < 0.05$)	U_{crit} ($P < 0.01$)
Fanta	13/07/04	0.46-0.56	0.42-0.46	9	3	70.0	8.0	2.0	25.0	2	0
Fanta	21/07/04	0.42-0.51	0.40-0.41	9	3	72.0	6.0	0.0	27.0	2	0
Coke	19/07/04	0.43-0.50	0.40-0.46	20	5	290.0	37.0	20.0	78.0	20	5
Coke	04/08/04	0.50-0.72	0.46-0.57	16	4	188.5	21.5	11.5	52.5	11	13

The calculated *t* values show in Table 30 were all less than the critical *t* value at 99% confident level, 2.58 and 2.75 for 58 and 28 degree of freedom, Therefore the null hypothesis was retained. That is the results from two analytical methods were not significant different.

To confirm that the two sample preparation techniques were not significantly different at a wider range of concentration 1 to 5 mL acetaldehyde standard solutions were spiked into the bottles. They were analyzed by the conventional and proposed methods. The results (Table 32) from the two methods were then compared using *t*-test. The comparison histogram is shown in Figure 47.

The calculated *t* values (0.02, 0.26, 0.30, 1.05 and 2.06) were all less than the critical *t* value at 99% confident level, 4.60 for 4 degree of freedom, Therefore the null hypothesis was retained. That is the results from two analytical methods were not significant different.

Table 32 Acetaldehyde concentrations at various spike volume of acetaldehyde solution

Volume (μL)	Proposed method ($ng\ mL^{-1}$)					Conventional method ($ng\ mL^{-1}$)				
	1	2	3	4	5	1	2	3	4	5
1.0	137.6	147.0	142.7	144.4	150.7	136.1	139.1	127.4	137.2	145.4
2.0	225.1	228.3	246.6	228.9	232.3	227.9	228.3	243.6	220.2	227.2
3.0	297.6	314.6	313.5	304.6	316.0	281.0	308.2	318.8	313.0	315.3
4.0	373.9	381.4	427.3	388.1	414.4	373.5	404.8	419.1	382.0	404.1
5.0	456.4	487.1	468.9	457.1	505.9	461.8	490.6	486.9	488.8	482.3

* 5 replications, RSD < 10 %

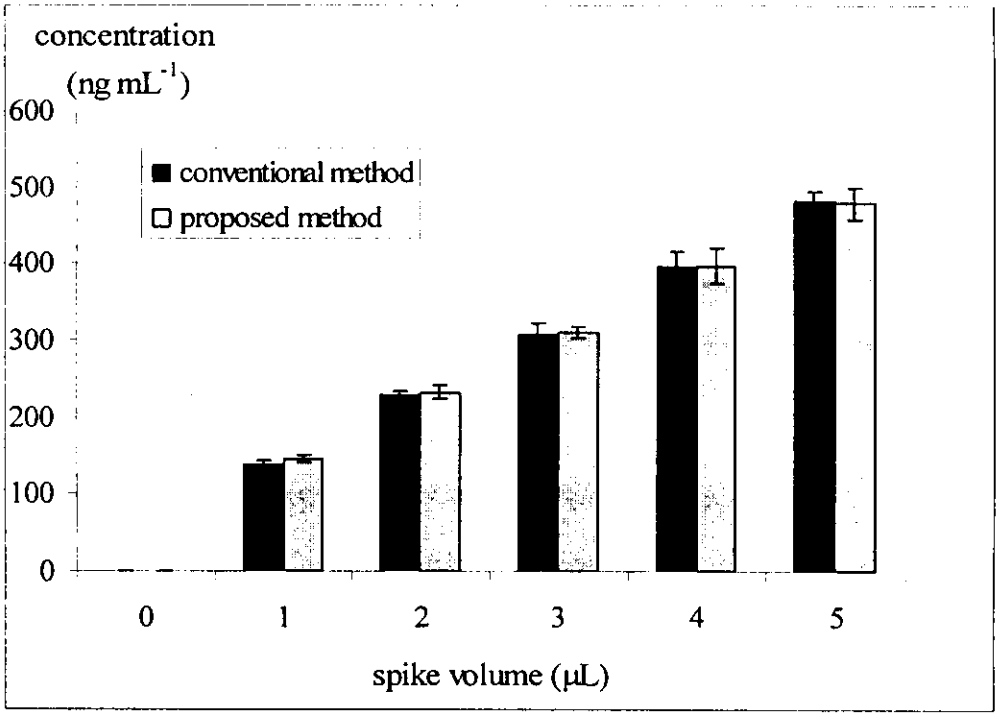


Figure 47 Histogram of conventional and proposed methods at various spike volumes of acetaldehyde solution

From the analysis, acetaldehyde residue in PET bottles was in the range of 0.4 to 1.1 ng mL^{-1}. These are less than the regulation of EU SCF, 6.8 mg kg^{-1} bottle weight (EU SCF, 1998) that equivalent to 3.51×10^8 ng mL^{-1} and also less than the specification from Coca-Cola Co., Ltd., 5 μg L^{-1} (5 ng mL^{-1}) (PET Guide, 2001).

The results also suggested that acetaldehyde concentrations migrated from PET bottle might also depend on the type of the resin. For 5015X resin from The PET and PET Pack, it produced the lowest acetaldehyde quantity, followed by the Indo PET from PET Asia, CB-608 from PET Far and Thai PET from PET Pack, respectively. The Viridian resin bottles from Kianjoo gave the highest concentrations.

For the supplier, comparing between The PET and PET Far (CB-608 resin), acetaldehyde that was migrated from freshly blown bottles were not different. Also the quantity of acetaldehyde of the 5015X resin from The PET and PET Pack were not different. The highest concentrations of acetaldehyde of the 22/05/47 PET FAR bottles were because of the molder of blowing process problem.

For the blowing temperature, a higher blowing temperature should produce higher amount of acetaldehyde residue in the bottle because acetaldehyde would come out during thermal degradation process of PET material. However, the results showed that the blowing temperature did not effect the concentrations because it is the optimized blowing temperature for each type of bottle of the company.

From these results, it seems that all resins and suppliers can be used.

3.12.2 Purge and Trap Technique

The results from the purge and trap technique were compared with the proposed method using Mann-Whitney U test (Miller and Miller, 2000; http:// www.physicalgeography.net/fundamentals/3g.htmL) and the results are shown in Table 31.

To test whether the two methods gave the same results, the null hypothesis was set, that is, there was no difference between the two methods. The results from two methods are first pooled and arranged in numerical order, but with one set of the results distinguished by underlining. Ranking the results and calculating the rank sum. The *U*-statistic value was then calculated by

$$U_1 = n_1 n_2 + \frac{n_1(n_1+1)}{2} - T_1$$

$$U_2 = n_1 n_2 + \frac{n_2(n_2+1)}{2} - T_2$$

where T_1 and T_2 are sum rank of method 1and method 2 results. The lower U-statistic value is the one used in the test to compare with the U- critical values. If the

U- calculated value is lower than the critical value, the null hypothesis is rejected. On the other hand if the the U- calculated value is greater than the critical value, the null hypothesis is retained (Miller and Miller, 2000; http:// www.physicalgeography.net/ fundamentals/ 3g.htmL).

From the results, U-calculated value were greater than the critical value, that is, the null hypothesis was retained, there was no different between the two methods at 99% confidence level.

Even though purge and trap technique was used to reduce the complication of sample transportation and preconcentration, it needed more time before analysis. After incubating the bottles for an hour, the proposed method could analyze the sample immediately. However, for the purge and trap technique it needed 15 minutes to purge the analyte through the adsorbent. Then a thermal desorption unit was required to desorb the analyte from the adsorbent. However, the analyte (adsorbed on adsorbent in adsorbent tube) can be stored for about one week before analysis. This is useful in the case where there is no enough time to analyze the sample immediately or when the laboratory is far away from the field.

These results showed that the proposed method can be used to analyze acetaldehyde residue in PET bottle. It can reduce the sample preparation time of conventional method from 24 hours to one hour. The advantages of this method were rapid, simple, no solvent needed, can be used in industry application and all sizes of the bottles can be analyzed. The purge and trap technique needed more time however it can be used to reduce the complication of sample transportation and also preconcentration.