



# Determination of Volatile Fatty Acids from Raw Natural Rubber Drying Activity by Thermal Desorption-Gas Chromatography

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Malodourous emission from raw natural rubber (NR) processing activities has become a public nuisance since residential and public development areas are gradually expanding near raw NR processing factories. The malodourous vapour mainly consists of volatile fatty acids (VFA) released from the breakdown of non-rubber constituents during drying stage of the raw rubber processing. An improved sampling methodology to characterise and monitor VFA from the drying stage was implemented. This study focused on the drying stage as the major source of malodour in the raw rubber processing. The thermal desorption-gas chromatography technique enabled direct sampling of air pollutants with minimal errors. It was found that acetic acid and propionic acids were present with highest concentrations. In general, concentrations of individual VFA varied throughout the drying stage. The raw NR processing factories were able to eliminate more than 71 % of total VFA using the relevant water scrubber treatment systems. The malodour characterization technique used in this study provides new technical information useful to develop more efficient malodour control systems for the raw NR processing industry.

## 1. Introduction

The raw natural rubber (NR) processing sector is one of key economic activities in Malaysia. The high demand of the NR worldwide contributed to the high rubber prices in recent years. However, the raw NR processing sector generates malodourous volatile organic compounds and increasingly becoming a public nuisance as public development areas are gradually expanding near raw NR processing factories. This problem is growing but has never been entirely solved. The malodourous vapour consists mainly of volatile fatty acids (VFA) as reported by Gan et al. (1975) and Yong et al. (1985). The VFA were produced during the breakdown of non-rubber constituents and released during the drying stage of in the rubber processing.

Relevant gas chromatography (GC) techniques have been widely used to identify individual components and determine their chemical concentrations using known standards of VFA. A sampling method was adopted by Gan et al (1975), Yong et al (1975) and Danteravanich (2007) using charcoal tube as an absorbent to collect VFA which were then condensed in chilled U-shape tube using dry ice. The absorbent and condensates were analyzed separately. The ideal sampling duration was two hours when using this type of sampling set-up. The trapped VFAs were extracted using ethyl acetate (EA) and subsequently centrifuged, filtered and injected into GC for detection against relevant VFA standards in EA. On the other hand, the condensates were injected directly into the GC analytical column and quantified for their concentrations using relevant VFA standards in water. The two

analyses would then give the total concentrations of VFAs in the exhaust vapour from the rubber drying stage.

This paper describes the use of advanced analytical equipment; thermal desorber (TD) called TD-GC technique for identifying and quantifying for monitoring purposes of the VFA. An active sampling method is administered, which uses sorbent tube as the sample collector. The volatile organic pollutants are retained in sorbent tube and are directly desorbed into thermal desorption unit to release the pollutants trapped into the GC for compound identification during analysis. The improved sampling methodology that incorporates active sampling technique saves on sampling time and requires no sample preparation. The results obtained should be more accurate and reliable due to few sources of errors. The active sampling technique developed is in accordance to the US EPA (1999) TO-17.

The objective of this study was to monitor VFA released from the drying stage of NR processing as a major contributor of organic pollutants and malodour in Malaysia. Zaid (2005) reported that malodour was being controlled by using water scrubber treatment systems (WSTS) adopted by most NR processing factories. The sampling procedure was divided into two parts consisting of a sampling prior to scrubber to sample vapours from the dryer and then a sampling after the scrubber to represent samples taken at the chimney of the water scrubber. Consequently the scrubbing efficiency could be readily determined. Organic pollutants were identified by using TD-GC coupled with Flame Ionization Detector (FID). The thermal desorber was used as a direct injection tool to desorb all organic pollutants trapped in sorbent tube during the sampling process. A comparison was also carried out for results obtained using this technique against the technique described in previous study by Danteravanich et al. (2007).

## **2. Materials and Methods**

### **2.1 Sorbent tube**

Self packed quartz tubes containing about 0.04 g Tenax TA<sup>®</sup> were activated by flowing nitrogen gas and heating at 300 - 350 °C for one hour for tube conditioning. The tubes were reconditioned each time before sampling to eliminate any possible trace of contaminants trapped during storage.

### **2.2 Sampling**

The exhaust air from the dryer was sampled at the inlet and outlet of the WSTS. Two stages of sampling system were applied where the air was first collected into the 10 L nalophan bag using a vacuum pump and eco-drum. Next, the air from the bag was pumped into the conditioned sorbent tube consist of Tenax TA<sup>®</sup> as absorbent material at controlled flow rate and the tube was detached from the pump and capped carefully prior to analysis (Figure 1). In this study, four replicates samples of before and after scrubbing were collected.

### **2.3 Chemical standard calibration**

An external calibration was performed where five points calibration curves were plotted by using a standard of mix volatile fatty acids manufactured by Supelco<sup>®</sup> consist of acetic, propionic, isobutyric, butyric, isovaleric, valeric, isocaproic, caproic and heptanoic acids. For each calibration point, the diluted liquid standard was loaded into the sorbent bed by using a syringe. A volume of 5 µL of each concentration ranging from 0.6 mM to 10 mM was injected and retained in the tube. Subsequently, the tube was desorbed immediately in the thermal desorber unit which is attached to the GC and the same desorption conditions were applied when analyse the sample.

### **2.4 VFA analysis**

The analysis was conducted using Perkin Elmer Clarus 600 (GC) attached with Turbo Matrix (TD). Volatile compounds contained in the samples are swept by a stream of inert gas to a cold trap, where they were re-concentrated in thermal desorber. At the end of this period, the cold trap was heated rapidly at a high temperature to release the volatiles to the GC analytical column.

The polar capillary column from Supelco<sup>®</sup> (Nukol<sup>TM</sup>) with specifications; 30 m length, 0.25 mm I.D and 0.25 µm thickness of particle size was used as a stationary phase. Nitrogen gas was used as carrier gas at flow rate of 1.0 mL/min. The injection temperature was 300 °C into 200 °C oven temperature. The ramp was 10 °C /min, 4 min hold and at initial temperature of 100 °C. The resulting peaks were

matched against calibration curve and compound concentrations are calculated in parts per million (ppm).

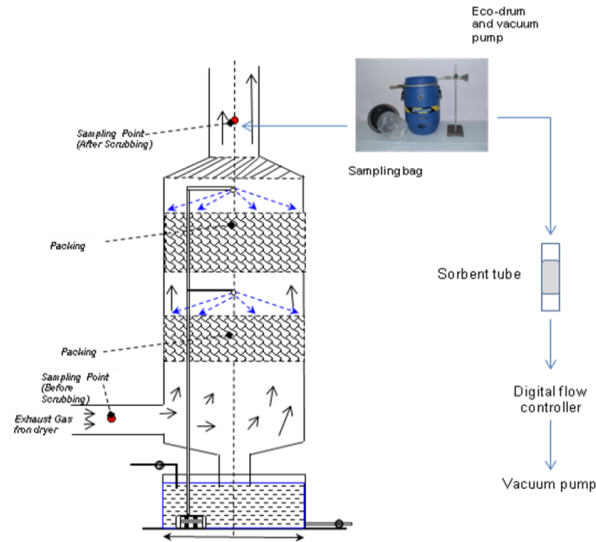


Figure 1: Two stages sampling train for vapour collection at WSTS

### 3. Results and Discussion

Figure 2 shows typical chromatograms obtained from TD-GC/FID analyses of samples from commercial NR processing factory before and after scrubbing with peaks mainly assigned to VFA. Table 1 shows the description of the respective VFA peaks assignment when identified against the calibration curve and their individual odour characteristics from literature by Merck Index (2006). The peak area was integrated for each VFA detected and the concentration was calculated accordingly. The concentrations range of VFA quantified are shown in Table 2.

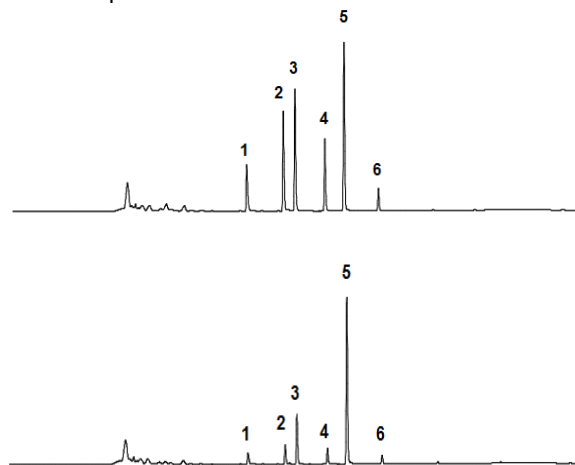


Figure 2: Typical chromatograms of VFA analyses obtained by TD-GC/FID before (top) and after (bottom) treatment using WSTS

Table 1: VFA peak descriptions from resulted chromatograms in Figure 2

| Peak No. | VFA             | Chemical formula   | Odour characteristic                  |
|----------|-----------------|--|---------------------------------------|
| 1        | Acetic acid     | CH <sub>3</sub> COOH   | Sewer taste and pungent odour         |
| 2        | Propionic acid  | CH <sub>3</sub> CH <sub>2</sub> COOH                                 | Clear liquid with pungent odour       |
| 3        | Isobutyric acid | CH <sub>3</sub> CH(CH <sub>3</sub> )COOH                             | Unpleasant odour                      |
| 4        | Butyric acid    | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH                 | Unpleasant odour and acrid taste      |
| 5        | Isovaleric acid | CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )COOH             | Strong pungent cheesy or sweaty smell |
| 6        | Valeric acid    | CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH | Very unpleasant odour                 |

The chromatograms obtained from scrubber samples before and after water scrubber system showed various peaks attributed mainly from VFA ranging from acetic to valeric acids. It was clearly observed that VFA was still detected after scrubbing despite being treated by water scrubber treatment system (WSTS). The VFA are known to have strong unpleasant odour characteristic even at the minimal concentration as stated by the characteristic of the VFA detected in Table 1. In principle, the WSTS removes the malodour by dissolving the organic pollutants that caused malodour through contact with water spray when entering the scrubber unit. Inert packing materials are placed inside the scrubber to increase the surface area so as to increase the residence time to promote mass transfer.

The results illustrated that acetic and propionic acids represented highest VFA concentrations in the exhausted vapour from the drying stage. This is evidently shown in Table 2 where the average concentrations of acetic acid before and after treatments are 977 ppm and 347 ppm while the concentration of propionic acid is 547 ppm and 214 ppm, respectively. In general, both types of VFA showed the average removal of 64 % and 61 % respectively. Furthermore, the higher molecular weight of VFA the lower the concentration detected. For instance, the concentration of valeric acid was merely 11 ppm before scrubbing and 5 ppm after scrubbing (Table 2).

Table 2: Summary of VFA detected in four replicates samples before and after scrubbing at a commercial NR processing factory

| VFA             | Samples from factories |              |                        |              | Average removal (%) |
|-----------------|------------------------|--------------|------------------------|--------------|---------------------|
|                 | Inlet water scrubbing  |              | Outlet water scrubbing |              |                     |
|                 | Range (ppm)            | Average ± SD | Range (ppm)            | Average ± SD |                     |
| Acetic acid     | 149-1703               | 977 ± 709    | 59-965                 | 347 ± 430    | 64                  |
| Propionic acid  | 101-996                | 549 ± 383    | 10-210                 | 214 ± 291    | 61                  |
| Isobutyric acid | 42-646                 | 307 ± 252    | 6-16                   | 10 ± 5       | 97                  |
| Butyric acid    | 8-263                  | 108 ± 109    | 5-11                   | 7 ± 3        | 94                  |
| Isovaleric acid | 17-330                 | 132 ± 134    | 12-36                  | 22 ± 11      | 83                  |
| Valeric acid    | 4-21                   | 11 ± 9       | 4-5                    | 5 ± 0.7      | 55                  |

It was observed as well that VFA with high molecular weights such as isovaleric and valeric acids showed lower solubility in water indicated by considerably low abundance reduction even though the corresponding average removal percentage was fairly high. In essence, one should have an impression that the acids should be completely eliminated looking at the small abundance when compared with VFA of lower molecular weights. In addition, the odour intensity of a VFA was directly proportional to its molecular weight as reported by Merck Index (2006).

This provides support that despite at low concentrations, the odour intensity emitted by VFA with high molecular weights is comparable to that of VFA with lower molecular weights but in abundance. Nevertheless, the result generally show a variation in concentration for the individual VFA detected throughout the drying process. The variation was partly attributed to vapour form of the samples as the calibration curve generated using a standard VFA cocktail exhibited a good reproducibility.

Furthermore, it can be observed from the analysis that WSTS adopted by the factory was able to eliminate about 71 % of VFA generated from the drying stage (Table 3). A further comparison of analytical results between the TD-GC method with the conventional GC method as reported by Danteravanich et al. (2007) is given in Table 4. The results showed that the TD-GC technique was more sensitive than the conventional GC method, as it was able to detect major VFA at a lower detection range. The direct sampling and sample injection technique was able to minimize the loss of compound and reflected a better preservation of samples prior to analysis whereby the compounds trapped inside the TD were retained for a longer time. The solid sorbent material does not alter the compound of interest and allow it to be desorbed easily during analysis.

Table 3: WSTS efficiency of total VFA removal

| Sample   | Total VFA concentration |                 | % Average VFA removal                                 |
|----------|-------------------------|-----------------|---|
|          | Before scrubbing        | After scrubbing |   |
| Sample 1 | 2516                    | 1628            | = $\frac{2081-604}{2081} \times 100$ %<br><b>71 %</b> |
| Sample 2 | 317                     | 113             |   |
| Sample 3 | 2587                    | 548             |   |
| Sample 4 | 2902                    | 125             |   |
| Average  | 2081                    | 604             |   |

Table 4: Comparison of average results obtained using TD-GC method and GC method with sample preparation as described in Danteravanich et al. (2007)

| VFA             | Total VFA concentration (ppm) |                       |                        |                       |
|-----------------|-------------------------------|-----------------------|------------------------|-----------------------|
|                 | TD-GC                         |                       | GC                     |                       |
|                 | Before scrubbing (ppm)        | After scrubbing (ppm) | Before scrubbing (ppm) | After scrubbing (ppm) |
| Acetic acid     | 977                           | 171.04                | 347                    | 20.52                 |
| Propionic acid  | 549                           | -                     | 214                    | 8.39                  |
| Isobutyric acid | 307                           | 8.56                  | 10                     | -                     |
| Butyric acid    | 108                           | 38.10                 | 7                      | 25.72                 |
| Isovaleric acid | 132                           | 21.39                 | 22                     | 13.89                 |
| Valeric acid    | 11                            | -                     | 5                      | -                     |

#### 4. Conclusions

The sampling and analysis of air samples from NR processing factories were determined quantitatively using a TD-GC/FID technique. The study showed the organic pollutants from the drying stage of the rubber processing were contributed by volatiles fatty acids (VFA) mainly acetic and propionic acids. It was observed that the WSTS installed by the factory was able to remove about 71 % of the total VFA and concentrations of VFA varied throughout the drying stage. Nevertheless, the sample replicates showed similar trend of individual VFA abundance.

The new active sampling of malodour into sorbent tube technique coupled with analytical method using TD-GC was able to reduce sampling duration and improved analysis tremendously where high sensitivity and good resolution of GC chromatograms were achieved.

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