Determination of methanol in pulp washing filtrates by desiccated full evaporation headspace gas chromatography

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ABSTRACT

This paper reports on a desiccated full evaporation headspace gas chromatographic (FE HS-GC) technique for determination of the methanol content in dilute mill effluents. Anhydrous K_2CO_3 was selected as the preferred salt for eliminating the water in the sample in the headspace sample vial. The results showed that the addition of 12 g K_2CO_3 made it possible to introduce a larger sample size (up to 1 mL) into the FE HS-GC measurement, thereby increasing the sensitivity of the technique. At the given equilibration temperature (105 °C), a near-complete mass transfer of methanol from the liquid phase to vapor phase (headspace) was achieved within 10 min. Replicate samples showed that the relative standard deviation of the method was less than 1.5%. Further, the limit of quantification (LOQ) was 0.12 μg and the recovery ranged from 95 to 104%. The present method greatly improves the methanol detection sensitivity in the FE HS-GC method and has the added advantage of being simple, rapid and accurate.

1. Introduction

Methanol, listed as a hazardous air pollutant by US Environmental Protection Agency [1], is the major volatile organic compound (VOC) released during industrial alkaline pulping and bleaching processes. The open facilities – such as screen system, decker system, washer system, blow tank, and pulp storage tank – are the major sites of release of methanol into the air [2]. Therefore, the determination of methanol content in the streams at these sites is particularly important to the predicting in the location of major methanol emissions [3,4]. Such information provides useful guidance when considering process controls.

In previous work, we developed two headspace gas chromatographic (HS-GC) methods (i.e., the conventional [5] and full evaporation (FE) [6]) for the determination of methanol in pulping spent liquors. The great advantage of HS-GC method is that it eliminates the sample pretreatment procedures [7] (to address sample matrix effects) required in the GC-based method proposed by The National Council for Air and Stream Improvement (NCASI) [8]. The conventional HS-GC method has been successfully applied to the analysis of methanol in various black liquors (pulping spent liquor) in a DOE sponsored project [9] and in oxygen delignification spent liquors, in which the methanol contents are relatively

high (200–2000 ppm). Since FE HS-GC method can significantly reduced the equilibrium time in headspace analysis (through the use of a very small sample size), it makes the methanol testing much more efficient than the conventional HS-GC method, without sacrificing detection sensitivity [6]. Unfortunately, neither method is suitable for quantifying the low concentration methanol (less than 200 ppm) in many dilute effluents (typically the washing filtrates of bleached pulps), which is unmanageable because of the high throughout [3,4]. Therefore, it is necessary to develop a sensitive analytical method that is able to quantify the low amount of methanol in these mill streams.

In previous studies [10], we found that the addition of inorganic salt in the sample solution is an effective way to enhance the Henry's law constant of methanol. However, even in a saturated solution of sodium carbonate (at 70 °C), the signal in the conventional HS-GC measurement was only about 4 times higher than that of a salt-free solution [11]. Although the analyte is nearly completely released into the headspace in the FE HS-GC method [6], the liquid sample size introduced must be very small (<30 μL) so that a near-complete evaporation in the closed headspace sample vial can be achieved. Obviously, using such small sample size also limits its capability for detecting the lower amounts of methanol in these dilute mill effluents.

The objective of the present work was to develop a desiccated FE HS-GC method for the determination of the low amount of methanol in washing filtrate samples. The main focus was on improving the detection sensitivity by the introduction of a larger

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sample size into the testing procedure. The precision and accuracy for the proposed methanol quantification method were also evaluated.

2. Experimental

2.1. Chemicals and samples

All chemicals including methanol, anhydrous K_2CO_3 and Na_2CO_3 used in the experiment were analytical grade and purchased from commercial sources. A standard methanol solution (1070 ppm) was prepared by adding 0.2684 g of pure methanol to 250 mL of distilled water.

A washing filtrate sample was obtained from a lab-scale oxygen delignification process.

2.2. Apparatus and operations

HS-GC measurements were carried out with an automatic headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, USA) equipped with a flame ionization detector and a DB-5 capillary column operating at a temperature of 30 °C with nitrogen carrier gas (flow rate = 3.8 mL/min). Headspace operating conditions were as follows: 10 min strong shaking for the sample equilibration at 105 °C; vial pressurization time = 0.2 min; and sample loop fill time = 0.2 min. Differential scanning calorimetric (DSC) measurements were carried out with DSC Analyzer (Netzsch DSC 204 F1, Germany), in which the heating rate operating was 4 °C/min.

3. Results and discussion

3.1. Elimination of liquid water by forming crystal hydrates

It is well known that water can react to form hydrate(s) of many inorganic salt crystals [12]. If the amount of salt is sufficient, the water in sample can be completely removed through the formation of solid crystal hydrate(s). Therefore, the liquid water phase in a closed sample vial, for example, can be eliminated.

In the present study, anhydrous K_2CO_3 and Na_2CO_3 were used as the salts for desiccating the liquid during headspace equilibration. As seen in Fig. 1, the presence of the inorganic salts extend the linear range of the GC response to volume size; cf., the upper two linear salt-added curves in Fig. 1 with the non-linear salt-free curve at the bottom. The salt-added curves also increase the GC response slope. In short, the detection sensitivity of methanol can be greatly improved by the addition of these anhydrous salts.
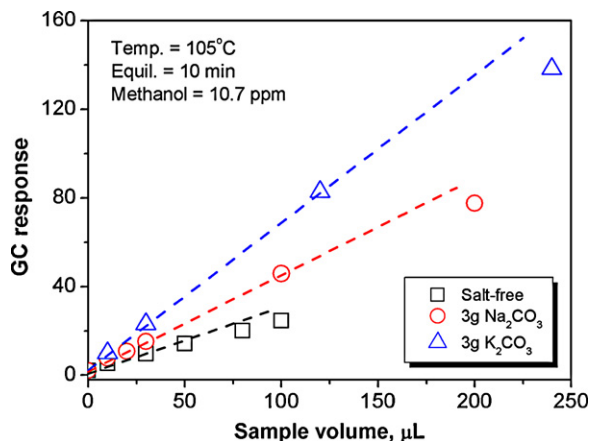

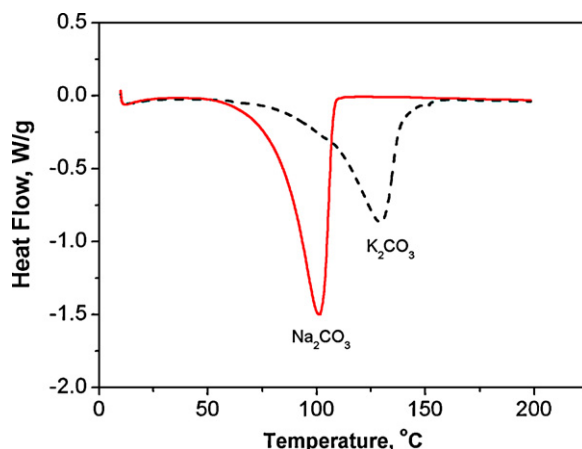**Fig. 1.** GC responses for methanol in samples with and without added anhydrous salts.

Fig. 2. DSC results for water-containing K_2CO_3 and Na_2CO_3 crystal samples.

Compared with the addition of K_2CO_3, the addition of Na_2CO_3 was found to be less effective in enhancing the GC response for methanol detection. In order to explore the cause for this phenomenon, DSC was used to exam both Na_2CO_3 and K_2CO_3 hydrate crystal samples, which were prepared by mixing 300 μL of water with 3 g of salt in a headspace sample vial for two hours at a room temperature. It was expected that at least part of the water was converted into the salt hydrate form during equilibration. As shown in Fig. 2, the releasing of the water added in K_2CO_3 sample required a higher temperature (130 °C) than that (101 °C) for the Na_2CO_3 sample. Therefore, K_2CO_3 is the better desiccant to use at the temperatures typically employed in FE HS-GC measurements (greater than 100 °C), since water in the Na_2CO_3 hydrate would be released even at the 105 °C equilibration temperature used in this experiment.

3.2. Evaluation of the completeness of methanol mass transfer

The completeness of methanol mass transfer in this desiccated method is related to several parameters [6]; i.e., equilibration temperature, equilibration time, liquid sample size and amount of salt introduced.

3.2.1. Equilibration temperature

Although a higher temperature could reduce the time required for equilibration, it would also create a higher pressure in the closed sample vial. As a result, the analyte in vapor phase would be more diluted due to the volume expansion during the headspace sampling through venting, which affects the detection sensitivity of the HS-GC method. As a compromise, 105 °C was selected as the equilibration temperature used in this study, as was done in previous studies [6,13–16].

3.2.2. Equilibration time

As shown in Fig. 3, the equilibrium of methanol in the vapor phase was achieved in about 10 min, which is longer than the equilibration time observed in the salt-free solutions in our previously reported work [6]. This behavior may reflect the fact that the contact area of the salt particles is limited so that a longer time is needed to completely adsorb the water. Based on the results displayed in Fig. 3, we chose 10 min as the time for equilibration in the present method.

3.2.3. Sample size

Fig. 4 shows the GC detection signal as a function of sample size for the original full evaporation procedure [6] and the enhanced, salt-added procedure used in this study. Note that the GC response
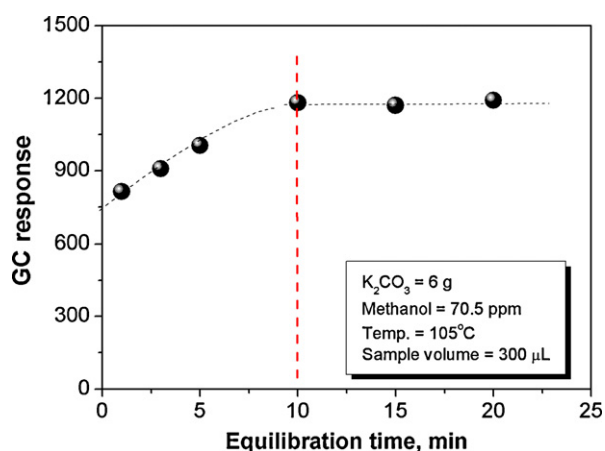
Fig. 3. Relationship between GC signal and equilibration time (sample size = 300 μL).

Fig. 5. Effect of the anhydrous K_2CO_3 dosage on the sample size-depended GC response linear range.

of methanol in the salt-free solution is actually non-linear, even within a very small volume range (<10 μL). This is because the vapor pressure of water at the given temperature and vial volume is proportional to the sample size. The total vapor pressure in the vial is mainly contributed by air and water in the vial, i.e.,

$$P_t = P_a + P_w \qquad (1)$$

where P_t, P_a, and P_w present the pressures of total, and caused by air and water vapor in the vial, respectively.

Since the sampling in this auto-headspace sampler is realized by venting the vapor to atmosphere through a sample coil, the higher pressure in the vial can lead to more vapor dilution during headspace sampling. It causes the non-linear response as showed in the inset of Fig. 4.

Clearly, the addition of K_2CO_3 increases both the linear range of the GC response and the response slope (i.e., sensitivity) in the methanol quantification.

3.2.4. The amount of K_2CO_3 added

In order to eliminate the free water in the headspace sample vial, a sufficient amount of anhydrous K_2CO_3 solid must be needed. Fig. 5 shows that for a given sample size (0.3 mL) a larger linear range of GC response can be achieved by adding a larger amount of K_2CO_3. According to Fig. 5 data, we can obtain an approximate relationship
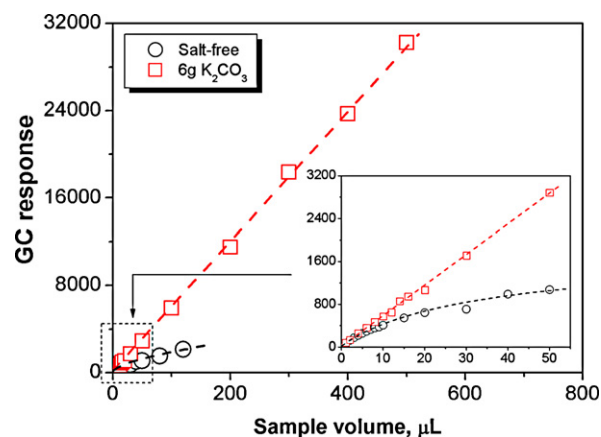

Fig. 4. GC linear response ranges of the salt-free and K_2CO_3 added samples (methanol = 1047 ppm).
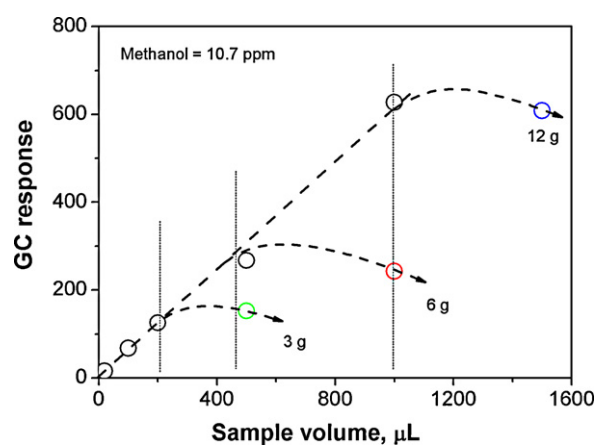
between the sample volume and the minimum amount of K_2CO_3 required, i.e.,

$$m_{K_2CO_3} \approx 0.012V \qquad (2)$$

where $m_{K_2CO_3}$ is the amount of anhydrous K_2CO_3 (in g) added and V is the volume (in μL) of sample in the headspace vial.

3.3. Method calibration and evaluation

A standard calibration curve was obtained using a set of solutions containing 0.1–10 ppm methanol. 500-μL samples of the solutions and 6 g K_2CO_3 were used in the HS-GC measurement. The equation of the standard calibration curve can be expressed as

$$A = 0.04(\pm 1.19) + 59.45(\pm 0.51) \times C \quad (n = 7, r^2 = 0.9995) \qquad (3)$$

where A is the GC signal of methanol detected and C is the sample size (in μg) introduced into the headspace sample vial.

The limit of quantitation (LOQ) for methanol in the salt-aided method is 0.12 μg, which is calculated by the following equation:

$$\text{LOQ} = \frac{a + 6 \times |\Delta a|}{s} \qquad (4)$$

where a, Δa and s represent the intercept, uncertainty of the intercept, and slope in Eq. (3), respectively.

Therefore, the LOQ in the present method is much lower than 3.29 μg found in a conventional FE HS-GC method calculated based on the data shown in Fig. 4.

The precision of the present method was evaluated by quintuplicate testing of two samples with methanol concentrations of 10.7 and 107 ppm, respectively. The results showed that the relative standard deviations were less than 1.5%.

To verify the use of this salt-added FE HS-GC method in practice, we prepared a set of sample solutions by accurately adding different amounts methanol to a washing filtrate and analyzing for the resulting methanol content using the present method. The net methanol concentration increases in the resulting solutions were in a range from 11.7 to 20.3 ppm. The washing filtrate of pulp after oxygen delignification (i.e., without adding methanol) was measured as a reference. Thus, the net signals due to the standard addition can be obtained, and the amount of the measured methanol in the samples can be calculated.

Table 1 compares the experimentally determined amounts using the salt-added method to the amounts of methanol actually added to the washing filtrate. Since the recovery data of the present method (listed in Table 1) are the range of 95.9–102%, we can conclude that the present technique is suitable for the quantification of methanol in washing filtrate samples.

Table 1
Method validation.[a]

Sample No.	Methanol content (ppm)		Recovery (%)
	Added	Measured	
1	2.15	2.06	95.8
2	5.37	5.48	102
3	6.44	6.67	104
4	8.59	8.65	101
5	10.7	10.9	102

[a] The methanol concentration in the original sample is 9.57 ppm.

4. Conclusions

A desiccated FE HS-GC technique for the determination of methanol in the diluted mill effluents has been developed. In the presence of anhydrous K_2CO_3, the sample size can be increased, thereby significantly decreasing the LOQ and increasing the detection sensitivity of the methanol analysis. The method has shown itself to be simple, rapid, and accurate.

Acknowledgements

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