

DETERMINATION OF TETRAHYDROTHIOPHENE IN AMBIENT AIR BY GAS CHROMATOGRAPHY WITH A PFPD DETECTOR COUPLED TO A PRECONCENTRATION TECHNOLOGY

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ABSTRACT

Tetrahydrothiophene (THT) is an odor additive used widely in the world. This paper introduced a new pre-concentration techniques coupled with a PFPD detector to analyze THT in ambient air samples. The positive results have been obtained in both standard and actual sample analysis. The results indicate that using Summa canisters or Tedlar bags to take the samples and followed by pre concentration techniques with a GC/PFPD detector, the lowest detection limits for THT can be as low as $2.0\mu\text{g}/\text{m}^3$. The relative standard deviations (n=6) of replicate sample precision are generally lower than 5.0%. Satisfactory results were obtained in the determination of THT in actual ambient air samples as well.

Key words:

Pre concentration techniques, PFPD, Summa canister, THT, ambient air

INTRODUCTION

Tetrahydrothiophene (THT) is a odor additive used widely by the developed countries in the world. It is commonly referred to as “add funk reagent”. To date, China has been using mercaptans (methyl mercaptan and ethyl mercaptan) as gas odor additives. However, THT is known for its more stable chemical characteristics as well as its ability to strongly resist for oxidation. In China plans are under way to substitute THT for mercaptans as an “add funk reagent”. However China currently lacks the methodology to analyze THT and mercaptans yet to its odor threshold level of one part per billion by volume (1 ppbv). Some studies [1],[2] have shown that pre concentration with a cryo focusing technology coupled with a GC/MS or other detector can achieve a sufficiently low-level volatile organic compounds (VOCs) detection limit in ambient air samples. The authors introduced this pre concentration technology with a GC/PFPD detector to analyze THT and mercaptans in ambient air samples. Multiple tests were performed to determine the ideal analytical conditions.

This method is based upon collection of whole air samples using SUMMA passivated stainless steel canisters or Tedlar bags. The canisters used for sampling were cleaned and pre-vacuumed prior to use. THT was isolated from the air sample by using a two-trap cryogenic pre concentration system with a second cryogenic on-column focus. Detection of THT was performed by a GC-PFPD. A satisfied result has been achieved for its high sensitivity and precision. The best pre concentration and GC condition are found in the experiment. This pre-concentration method appears to be an ideal method for detecting trace THT in ambient air.

EXPERIMENT

Instrument:

Gas chromatogram: HP6890 GC with PFPD detector.

Pre concentration system: Nutech 3550A.

Auto sampler: Nutech 3600

Sampling containers: Aerosphere™ 6L SUMMA canisters or 3L Tedlar bags and mini-sampling pump

Canister cleaning system: Cycle Clean Model # 214GP

Column: HP-GASPRO 60m×320µm

Standard:

Tetrahydrothiophene: GC grade

Internal standards: Bromochloromethane, 1,4-Difluorobenzene, Chlorobenzene-d5, and Bromofluorobenzene, all at concentration of 1 mg/m³

Balance gas: high purity nitrogen

Standard gas dilution:

Using a 10µL micro-syringe, inject certain amount of THT GC grade standard into a 6L SUMMA canister or 3L Tedlar bag to make a high concentration THT standard gas. Then use 100ml syringe to get 25ml, 50ml, 75ml, and 100ml high concentration THT standard gas and inject into 1L Tedlar bags to make a working standard gas. Injecting 400mL into pre concentrator system for each sample. Each level is repeated 3 times.

Pre concentrator Conditions:

Cryogenic pre concentrator system:

Cryotrap: cool: -150°C, heating: 150°C

Cryofocusing: cool: -150°C, heat: 150°C, heating rate: 99°C/min

Transfer line: 150°C, Load trap valve: 175°C, Analyze time: 25 min

GC Conditions:

Carrier gas: high purity helium(>99.999%)

Carrier gas flow: 1.0ml/min

Column temperature program: 35°C hold 8 min, 5°C/min to 180°C hold 5 min

Inlet mode: splitless

Inlet temperature: 200°C

PFPD temperature: 250°C

Hydrogen flow: 11.5 ml/min

Air 1 flow: 10.0 ml/min

Air 2 flow: 12.0 ml/min

Sample Collection:

The SUMMA canisters used for sampling are pre-vacuumed prior to use in the laboratory. For grab sampling, the canister valve is opened for one minute to allow sample air to be drawn into the canister. Close the valve after sampling. Flow controllers are used to obtain time interval ambient air samples. A mini-sampling pump is used to collect air samples into the Tedlar bags.

Sample container cleaning:

Before usage, SUMMA canisters and Tedlar bags must be cleaned using a special canister cleaning system. Heating jackets are wrapped around each canister (~100 °C). They are repeatedly filled with moist high purity nitrogen and pumped down using a diffusion pump and a turbo pump for a total of 8 cycles. From the batch of canisters cleaned, one canister is selected. It is filled with nitrogen and analyzed using a pre concentration system with GC/MS to check for the presence of any contamination. If the canister analysis is determined to be "clean", the canister is returned to the batch and the test canister is re-evacuated. All canisters in the batch are considered ready for sampling.

RESULTS AND DISCUSSION

Volume of sample selection:

The volume of sample needed is primarily determined by sample concentration, humidity and CO₂ content. For high humidity samples (humidity >65%), volume of less than 200ml is preferred. For regular ambient air samples 400 ml of sample can be injected into pre concentrator system in order to obtain better detection limit.

Concentrator temperature select:

Because of high boiling point of THT the first stage cryo trap temperature of -150 °C is selected for optimal trapping efficiency. Next, to set the second stage cryo-focus temperature at -160 °C to refocuses the sulfide before the inlet at the head of the column to improve peak shape.

Humidity and CO₂ infection:

The air sample usually contains moisture and CO₂. Without removing those, water and CO₂ coagulation will block the flow path, affect the column overloading and increasing hold time variability. To selectively remove the water and majority of the CO₂ from the air, the Nutech 3550A per concentrator contains a Nafion dryer and a trap flash. If there is excessive CO₂ in sample, Nafion dryer and trap flash will not be sufficient. The addition of a CO₂ absorption tube was found to further aid in reduction of CO₂ as well as moisture.

Detector sensitivity:

The mass spectrometer was operated in both the full scan and selected ion monitoring (SIM)

modes. The experiment consisted of injecting 500ug/m³ THT. Comparing the sensitivity of full scan versus SIM revealed that SIM mode was 10 times higher than the full scan mode.

The FPD detector sensitivity is a little higher than SIM method, which is 38µg/m³. But The PFPD detector sensitivity is about 20 times higher than FPD, around 2.0ug/m³. It can reach THT's odor threshold level. So the PFPD detector was found the best one for in determining trace THT in ambient air and is selected for the method.

Sampling container select:

Sulfide is easy adsorbed and oxidized by container surface. A stability study was performed using different type of containers with a concentration of 100 ug/m³ THT, As shown in Figure 1. This figure shows that SUMMA passivated stainless steel canisters and Tedlar bags both have better stability results. THT will remain stable for about 120 hours. But THT will not be stable in the aluminum bags and the glass syringes. Summa canister and Tedlar bags should be chosen for THT sampling.

Total Ion Chromatogram (TIC)

Under the conditions mentioned above, 400mL of 330g/m³ THT standard gas has been analyzed. Figure 2 shows the total ion chromatogram for THT standard gas. One can find that the THT is separated and identified well in this analysis. Figure 5 shows the total ion chromatogram of an actual ambient air sample which was taken from a harbor site where the liquid propane was loading & unloading. Low level THT was found in this ambient air sample and the separation and identification is clear.

Precision and sensitivity experiments

Table 1 tabulates the results for precision and sensitivity of THT standard gases under the above-mentioned operating conditions. It shows that for a average concentration of 50 ug/m³ the precision can be as good as 1.29% of RPD. And the 2.0 ug/m³ detection limit can be reached.

Table 1: Sensitivity & Precision of THT on Pre concentrator with GC/PFPD

Item	THT Results
Concentration of Standard Gas, ug/M ³	50
	47.9
	49.4
Replicate results, ug/M ³	50.2
	51.1
	48.9
	51.7
Average, ug/M ³	49.9
Relative standard deviation %	1.29
Minimum Detection Limit , ug/M ³	2.0

Samples analysis:

Nine ambient air samples were collected and analyzed by the optimized method. The first 3 samples were taken from the area around the harbor site where the liquid propane was loading & unloading. The second 3 samples were taken from the loading area right in the loading tanks of liquid propane. The third 3 samples were taken from ambient air of the city zone. All samples are analyzed by Nutech pre concentration system with a GC-PFPD. Table 2 tabulates the quantitative sample results. It shows that low level THT was found by this method in different area and the results for the different area are reasonable. Fig. 3 shows the total ion chromatogram of the ambient sample.

Table 2: The Testing Results of THT in Ambient Samples

Sample Number	Testing Results, ug/M ³
1	5.6
2	6.7
3	<2.0
4	8.1
5	7.6
6	4.3
7	<2.0
8	<2.0
9	<2.0

CONCLUSION

This study has shown that trace amounts of THT can be detected in ambient air samples by using the Nutech 3550A pre concentrator coupled with a GC/PFPD. This method has both better sensitivity and precision. The sensitivity, expressed as the method detection limit (MDL), was calculated to be 2.0µg/m³. This value is 20 times lower when compared to the FPD detector. This experiment mainly focused on identification and quantitation of THT. However, upon collection of whole air samples, other VOCs were also concentrated and cryo focused and can be seen as tentatively identified compounds (TICs). These VOCs can be quantified using the GC/MS system. This method may be suitable for monitoring different VOCs and other sulfur compounds in ambient air for both indoor and outdoor samples.

REFERANCE

- [1] U.S. EPA, 1999, Compendium Method for the determination of VOC_s in ambient air using Summa passivated canister sampling and GC analysis (Method TO-14A).
- [2] U.S. EPA, 1997, Compendium Method for the determination of VOCS in air using Collected in Specially-Prepared canisters And Analyzed By GC-MS (Method TO-15)
- [3] Bianchi AP, Varney MS Sampling and analysis of VOCS in estuarine air by GS-MS, J.of Chrom ,643,pp 11-23(1993)

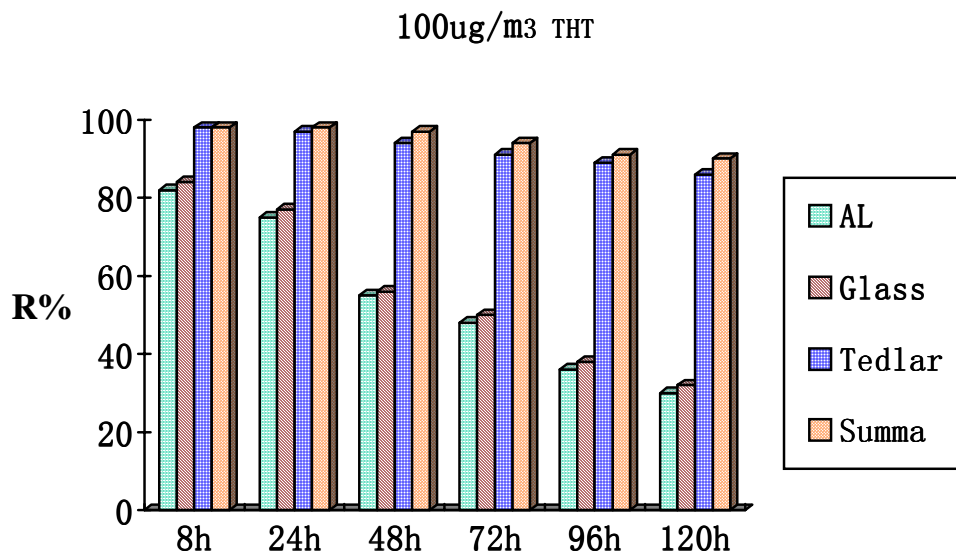


Fig. 1 The stability comparison of sampling containers

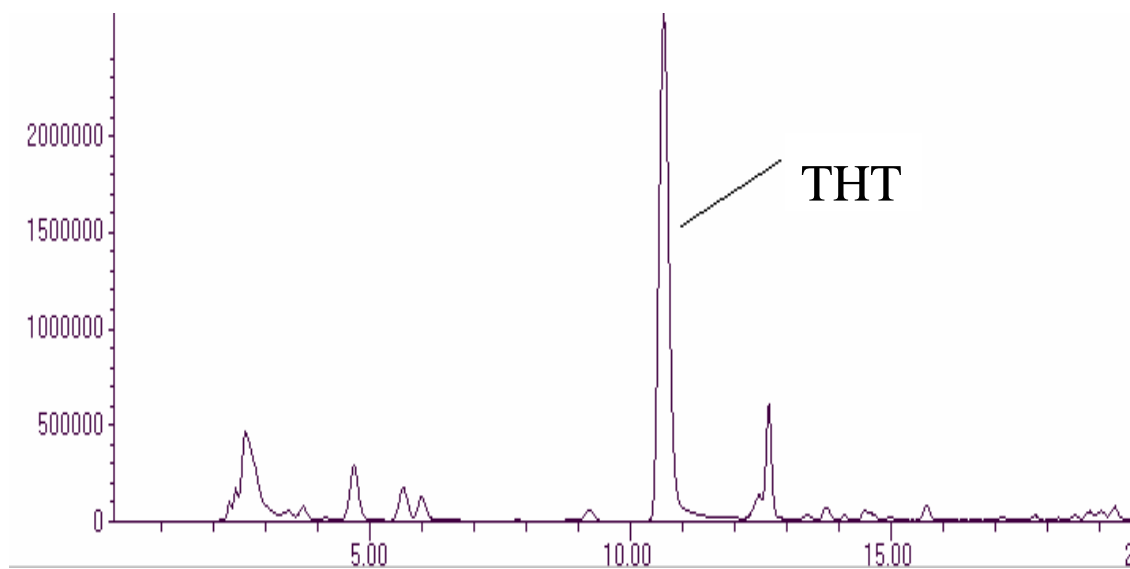


Fig. 2: TIC Chromatogram shows 330 ug/cu M Tetrahydrothiophene

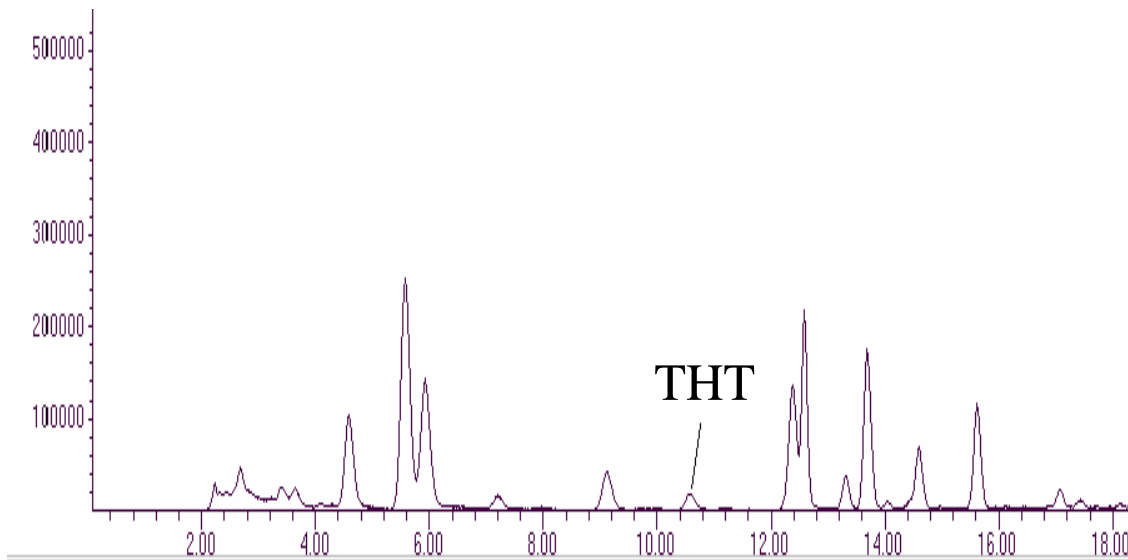


Fig. 3: The ambient sample taken from liquid propane quay shows THT