AIMES

analytical innovation measurement of environment samples

established in Germany 2001

established in Japan 2002

Motto

Analysis of well-defined compounds can be performed
in addition to the
existing method of „total" analysis.

AIMES

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A manuel purge and trap system (P&T)

A manual purge and trap system (P&T) for volatile organic substances (VOCs)

Introduction

Purge and trap system was setup and underwent a trial process. Purging process can release chemicals with high vapor pressure from liquid into gaseous phase at purger temperature. The purged chemicals are then be trapped at extreme low temperature to concentrate the sample before quantification. The purged chemicals are free from organic matrices that can avoid such interferences in quantification using GC-ECD, GC-MS or GC-HRMS.

Interest in fluorinated telomer alcohol ($CF_3(CF_2)nCH_2CH_2OH$) is increasing because FTOHs are suspected to be the precursors of perfluorinated compounds and they may degrade and give rise o perfluorinated compounds; and they are thought to be undergone long-range transport because of their volatility

Another group of chemicals, bromoforms ($CHBr_3$), can either be formed through biological or industrial processes

Principle of Method

Purge and trap system a dynamic headspace system. Chemicals with high vapor pressure will be introduced into gaseous phase by continuous gas (He) bubbling. All involatile components remain in the headspace vial and are not analyzed. Target chemicals bubbled out from the matrix are free of organic matrix interference, such that a better sensitivity can be obtained.

During purge phase, chemicals bubbled out will be trapped at low temperature -100°C. Unibeads can increase the surface area for the adsorption of volatile chemicals, continuous bubbling can disturb the equilibrium of the volatile chemicals between

liquid and gaseous phases. As the gas is moving to the vent, more and more volatile chemicals are then leaving liquid phase and they will then trapped/concentrated onto unibead surface.

At desorption phase, volatile chemicals will be released at high temperature (60-90°C) and they are then trapped in 2nd trapped in order to condense all the compounds before injection onto GC column. The 2nd trap is important because chemicals leave from 1st trap take 3-4min, if direct injection proceeds, tailing of peak will be observed. Before direct injection, chemicals are further trapped into 2nd trap and the releasing time from the second trap takes only 2-5 sec that can result in a better resolution for GC chromatogram.

Materials

1. Glass purger ~90mL volume;
2. Nafion drying tube, Ansyco MD 050-12P-2
3. Capillary – Restexk, Phase: RTX-VGC, 60m, ID 0.25, DF 1.4µm
4. 6 port Valco Valve;
5. Connector with ferrule;
6. Insulating box;
7. Alumina box with two temperature zone

a) minus 70°C

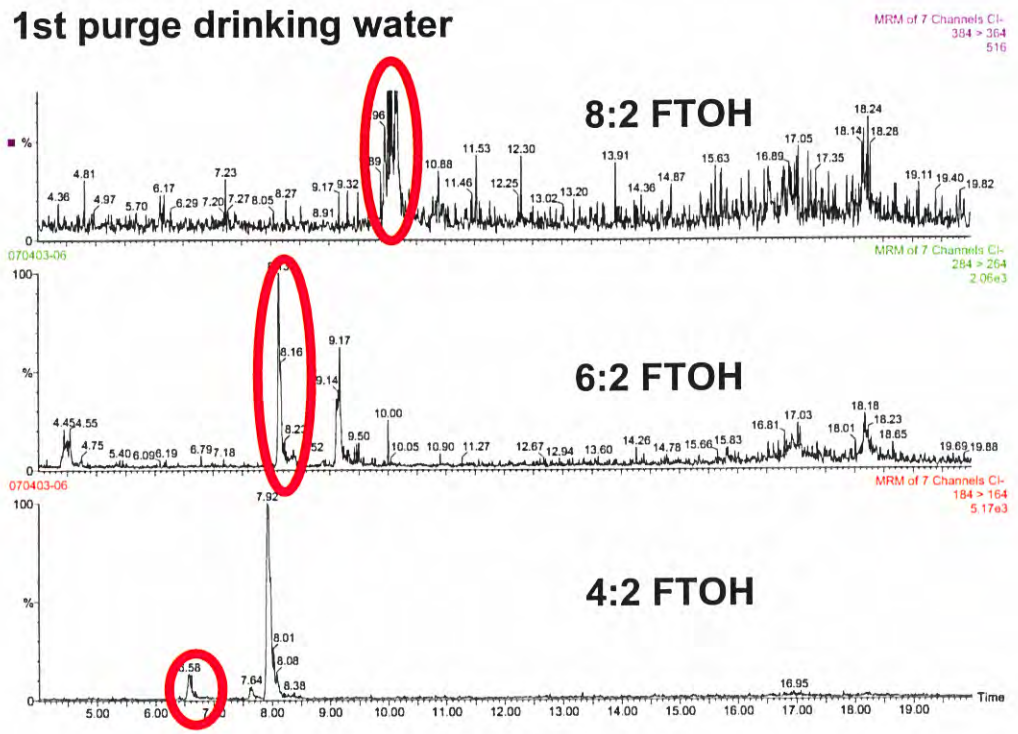
b) plus 100°C

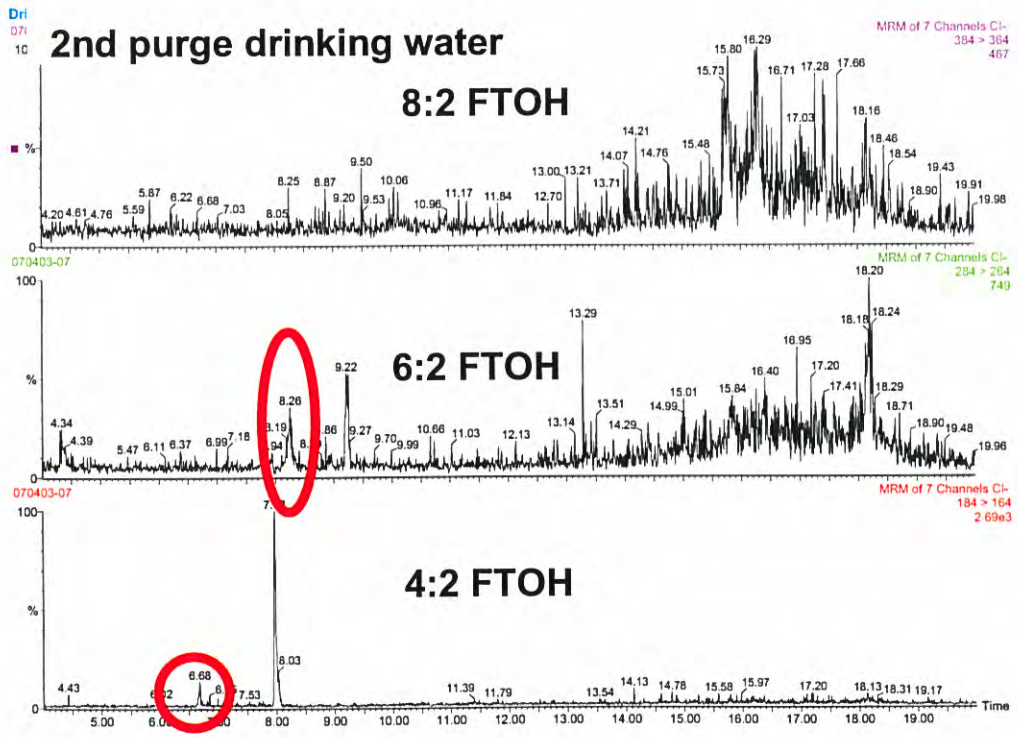
8. Glass rod filled with unibeads;
9. all connection are fused silica, non polar deactivated
10. Gas controller x 3 - sample injector, Nafion drying tube, purger;
11. Temperature controllers and sensors x 3 – purger, valve, insulating box
12. Sample bottle;
13. two way switches x 3 – sample injector (2 switch), Nafion drying tube (2 on/off switch), purger (one on/off switch);

Important points:

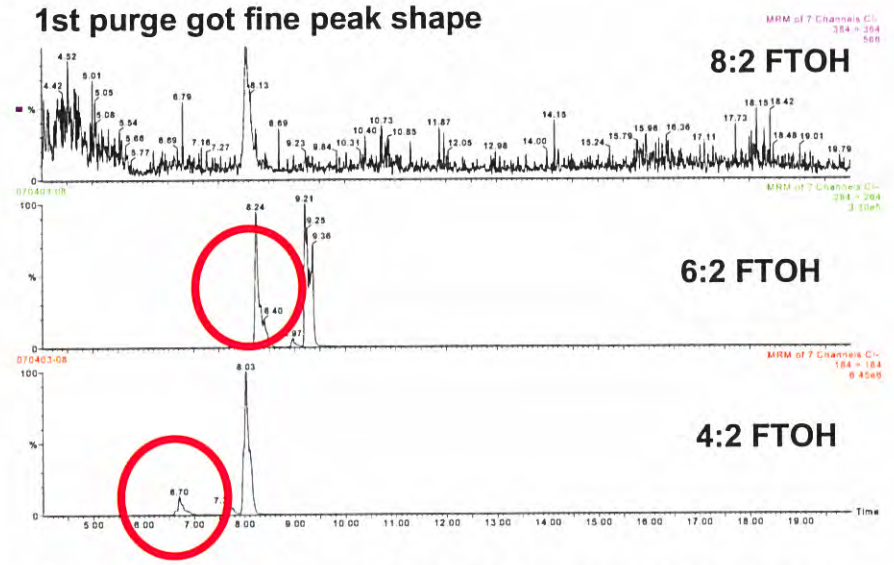
1. Extreme low temperature is required to trap the volatile chemicals;
2. Constant temperature is required during introduction of chemicals onto GC column;
3. Chemicals with high vapor pressure will come out first and but chemicals with low vapor pressure need further adjustment, i.e. purging temperature, purging time, etc.
4. Samples with foam formation need some adjustments. Option 1: Reduce sample volume such that dead volume in the purger can increase that can prevent foam getting into the capillary. Option 2: Connect a glass bulb to increase dead volume to trap the foam formed during purging. Both 1 and 2 are possible solutions, however, an increase in dead volume that more time is needed for pu

1. Drinking water was purged

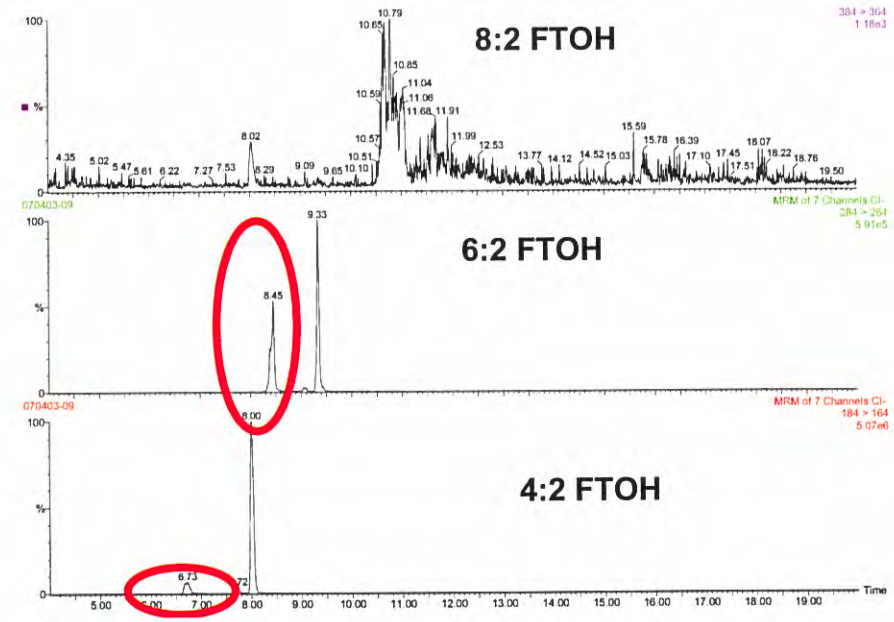


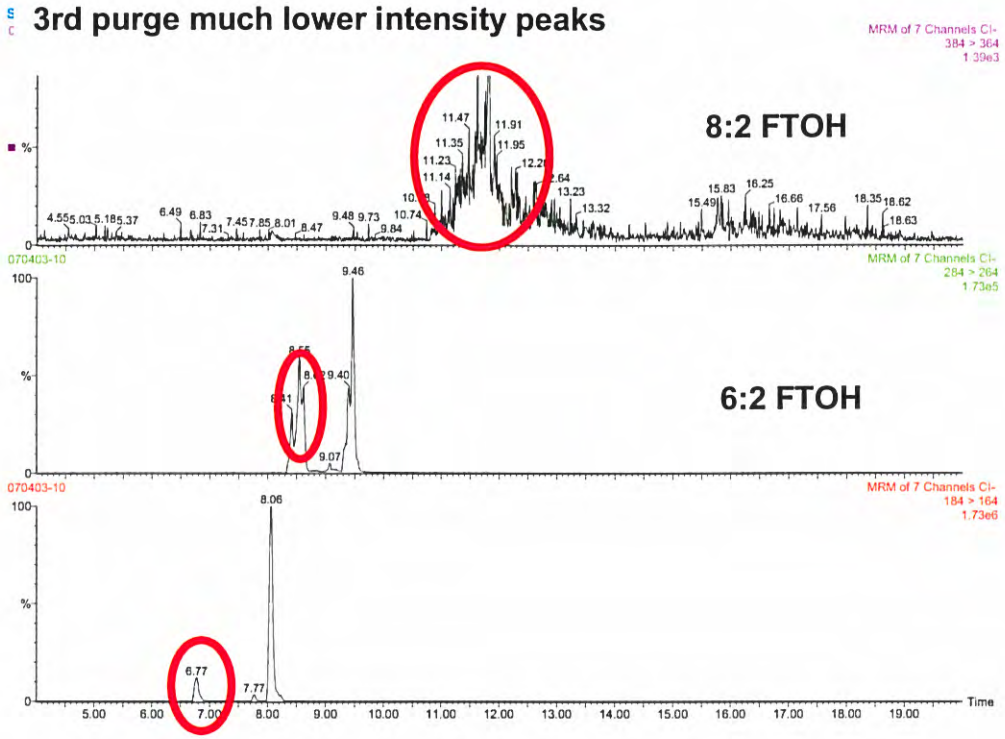


2. Spike standard into drinking water



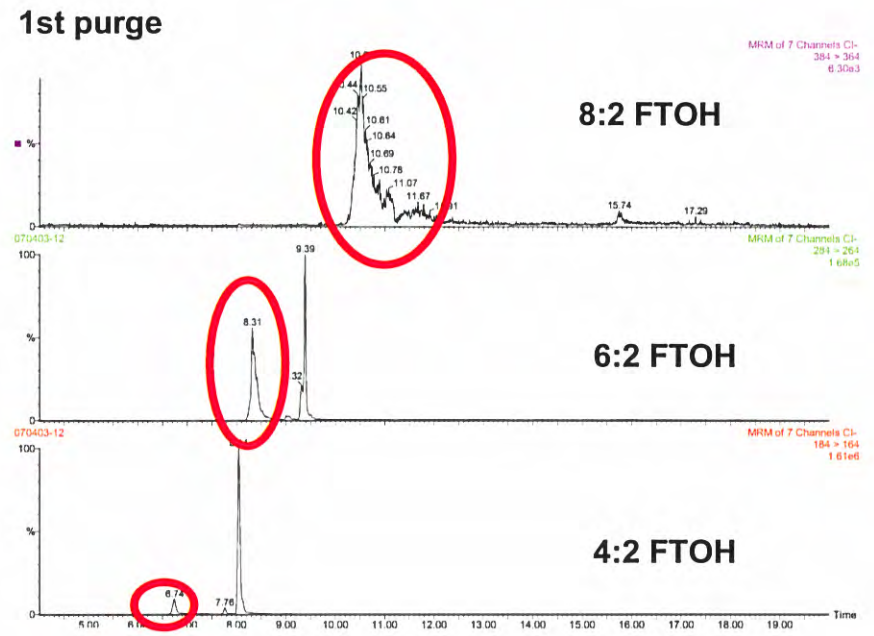
2nd purge got fine peak shape and lower intensity than those of the previous one.

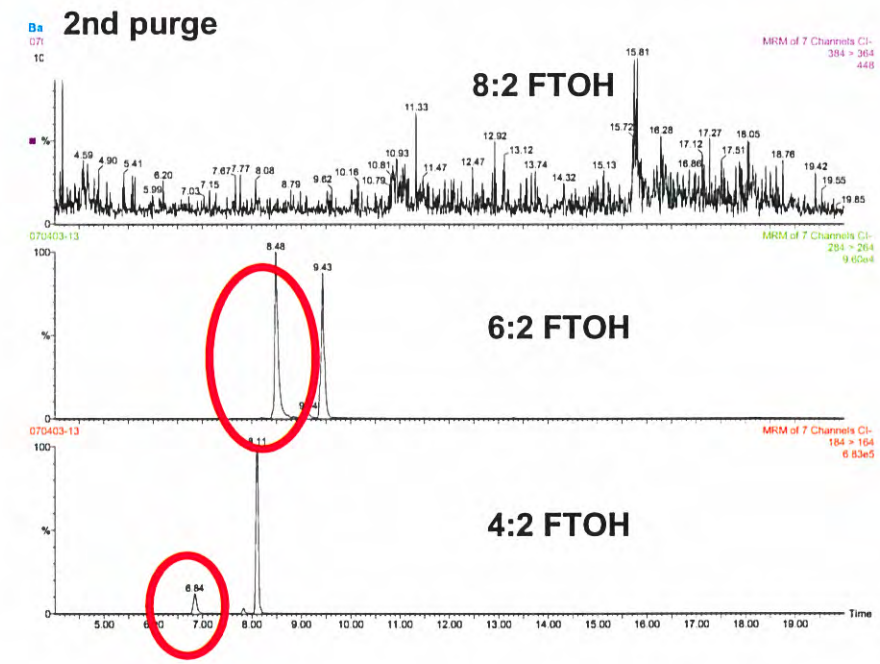




III.

1. Baltic water was purged





B. Injection of bromoform using purge and trap system onto GC-HRMS

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Analytical method:

GC column: DB-6 (60 m × 0.25 mm i.d. × 0.25 µm)

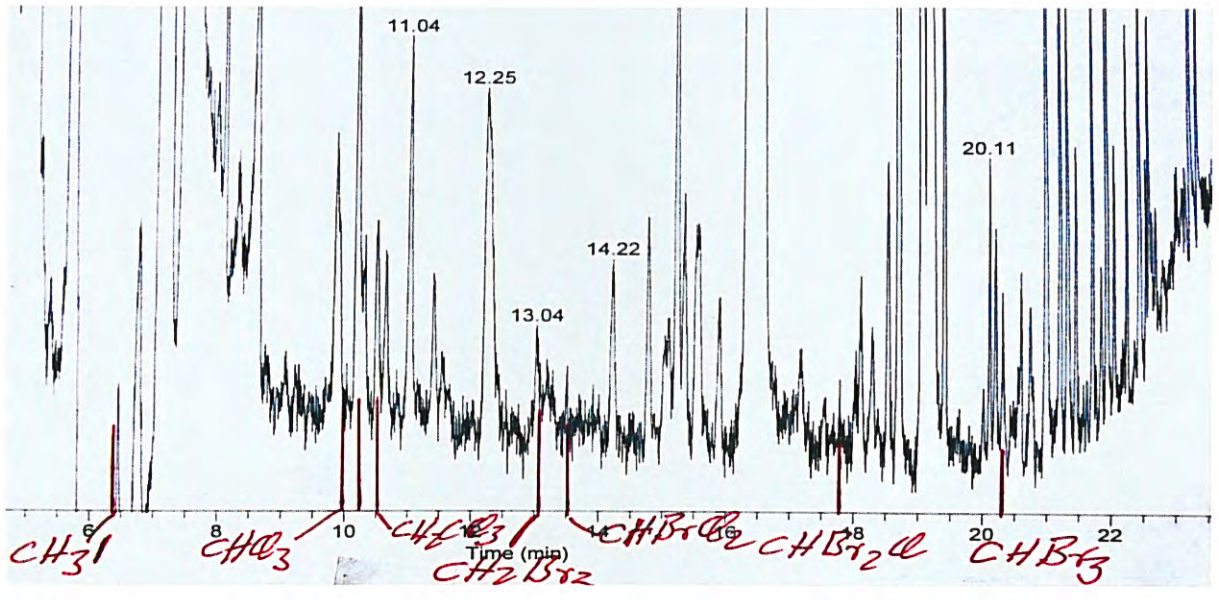
GC method: 35 °C (3 min) → (4 °C/min) → 85 °C (1 min)→ (15 °C/min)

→ 160 °C →(20 °C/min) → 180 °C (2.5 min)

North Atlantic water (10l) purge, 20 min 25ml/min

MS: scan mode 45-450 msu

GC: 35°, 3min, 6°C/min to 200°C



many of substances are at the purge gas

the" Bromos" represent only few percentages of the total amount

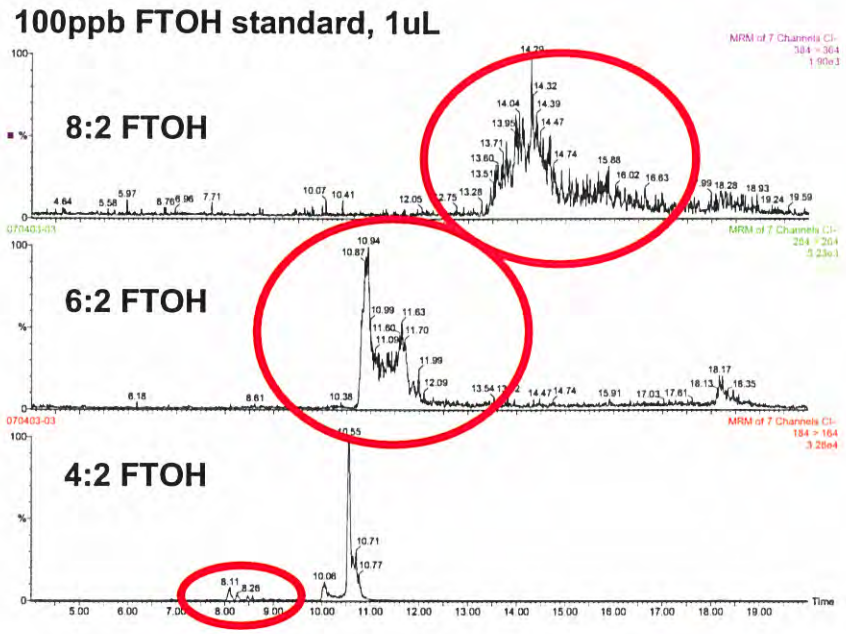
Conclusion

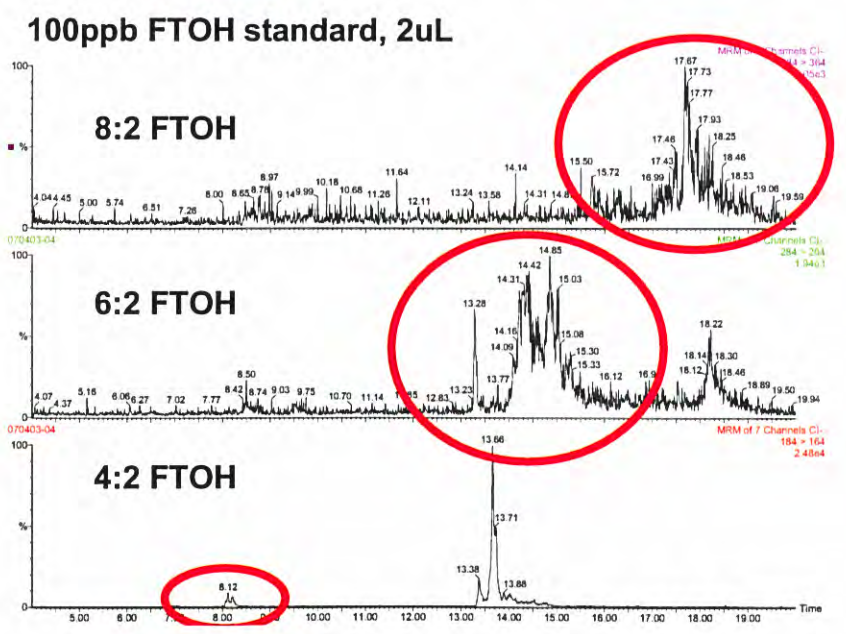
In the present experiment, we could demonstrate the use of purge and trap system to identify 4:2, 6:2 FTOH using GCMSMS and different "Bromos" using HRGC-HRMS. Further experiments are required to optimize the methods.

1. Repeatability of purge and trap system;
2. Recovery of purge and trap system;
3. Blank of purge and trap system.

1. Direct injection on GC via EPC, valve was at injection position.

1. **100ppb, 1uL/2uL in CH_3OH onto GC resulted in poor peak shape and intensity.**



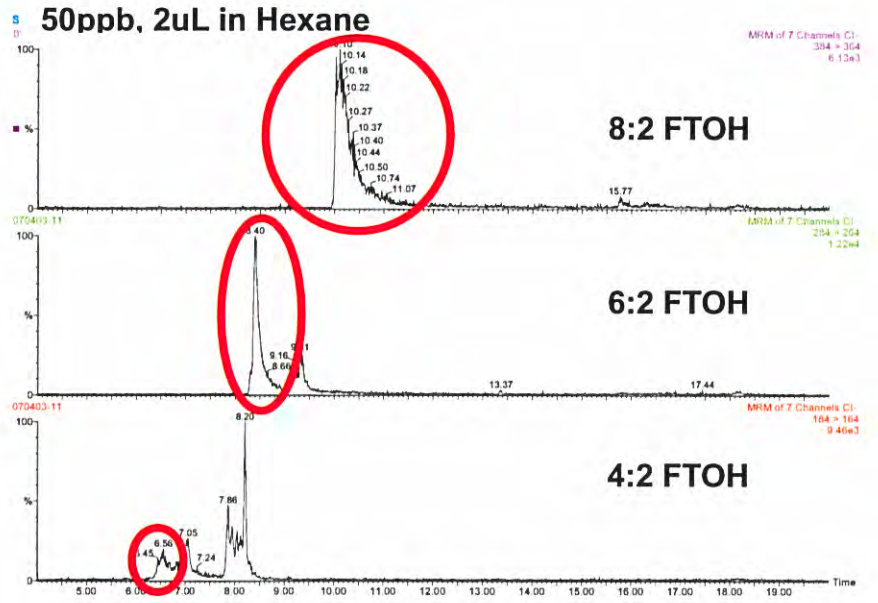


a. FTOH, MeOH are polar compounds whereas DB-WAX is also a polar column that might result in weak retention for the compounds.

b. Non-polar solvent was suggested for FTOH.

2. Direct injection on GC, valve was at trap position, shortcut

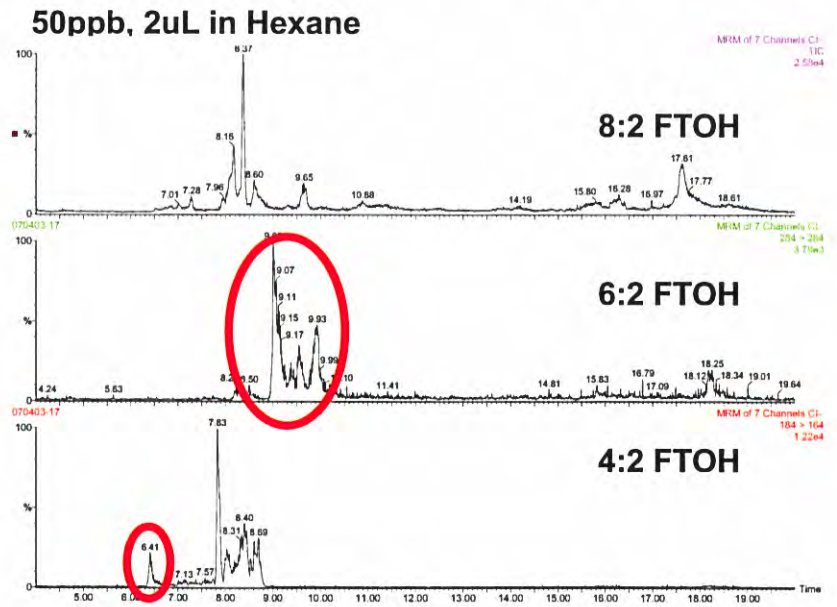
1. 50ppb, 2uL in Hexane onto GC also resulted in poor peak shape and intensity.



a. Try using trap system.

3. Direct injection on valve and standard was trapped in the 2nd trap, valve was at injection position.

1. 50ppb, 2uL in Hexane onto GC also resulted in poor peak shape and intensity.



a. Injection port (Direct from EPC) was suspected that had some problems.

at injection position (Figure 2c). Release the trap from liquid nitrogen, and target chemicals will then be introduced onto GC column according GC method and will then be detected by tandem MS or high resolution MS (HRMS).

Figure 2b

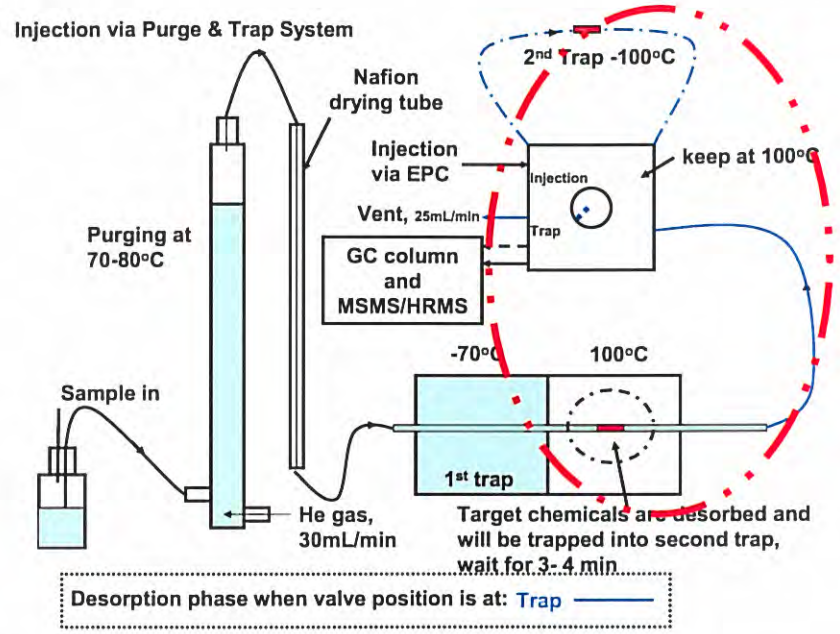
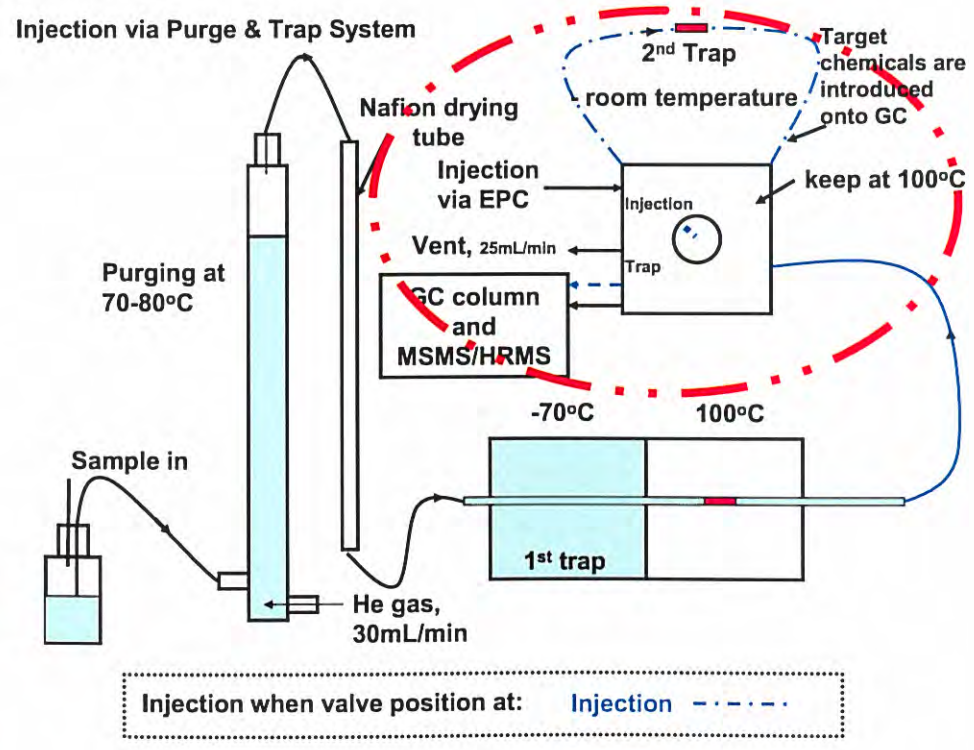


Figure 2c



Injection between samples

Firstly, desorb the unibeads for 3min and then cool down for further 3 min. Drain out the sample using switch and fill up the sample by applying pressure to the sample injector using switch. Around 90mL will be introduced into the purger. Observe the level of the sample, be careful of the overflow or introduction of the sample into Nafion drying tube because it will cause high back pressure or might introduce some water into the unibeads that might be frozen at -70°C.

Results and Discussion

Trial Programme

A. Injection of FTOH using purge and trap system onto GC-MS/MS;

B. Injection of bromoform using purge and trap system onto GC-HRMS.

A. Injection of FTOH using purge and trap system onto GC-MS/MS

Analytical method

GC column: DB-WAX (30 m × 0.25 mm i.d. × 0.25 μm)

GC method: 60 °C (1 min) → (3 °C/min) → 75 °C → (5 °C/min) → 170 °C → (20 °C/min) → 230 °C → (20 °C/min) → 250 °C (3 min)

Mass method:

Ion mode: Negative CI

Monitor ion: 184 > 164 (4:2 FTOH),

284 > 264 (6:2 FTOH),

384 > 364 (8:2 FTOH)

Purge and Trap system operation manual

Injection of sample using EPC has two injection options:

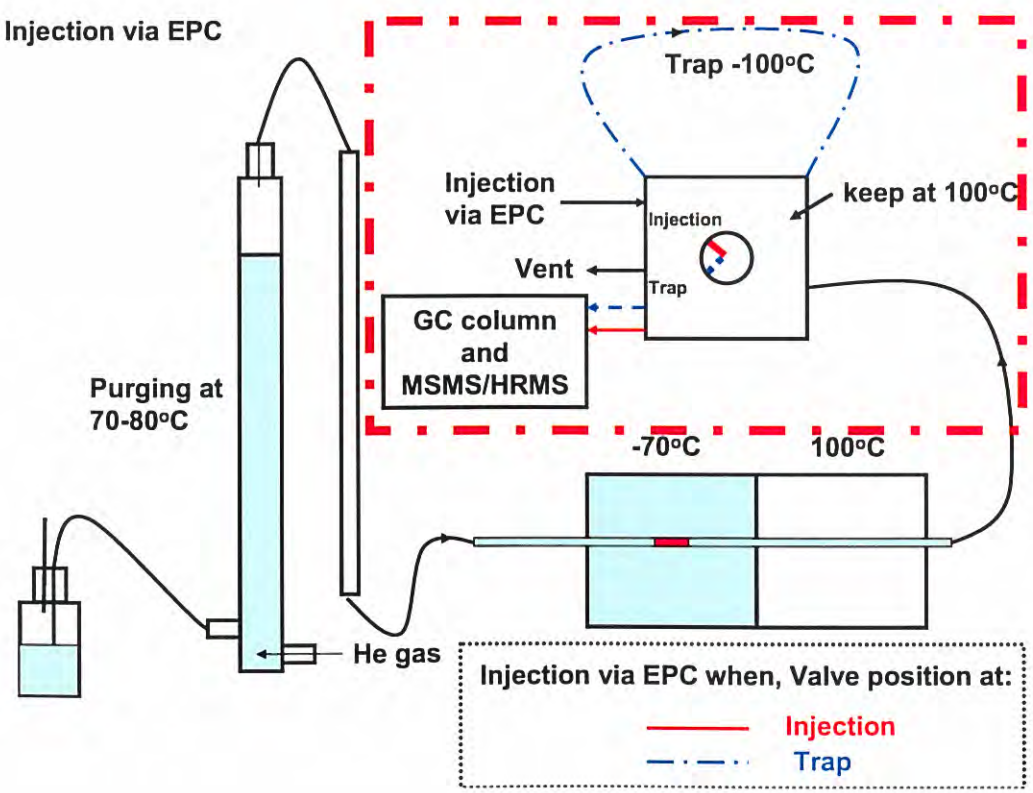
Scenario 1 (Injection via EPC) (Figure 1, red line):

When the valve is at the **injection** position, sample injected via EPC will be directly injected onto GC column according GC method and will then be detected by tandem MS or high resolution MS (HRMS).

Scenario 2 (Injection via EPC) (Figure 1, blue dash line):

When the valve is at the **trap** position, sample injected via EPC will be trapped at -100°C. To inject the sample, firstly, turn the valve at injection position, and then remove the trap from liquid nitrogen. Sample will be introduced onto GC column according GC method and will then be detected by tandem MS or high resolution MS (HRMS).

Figure 1.

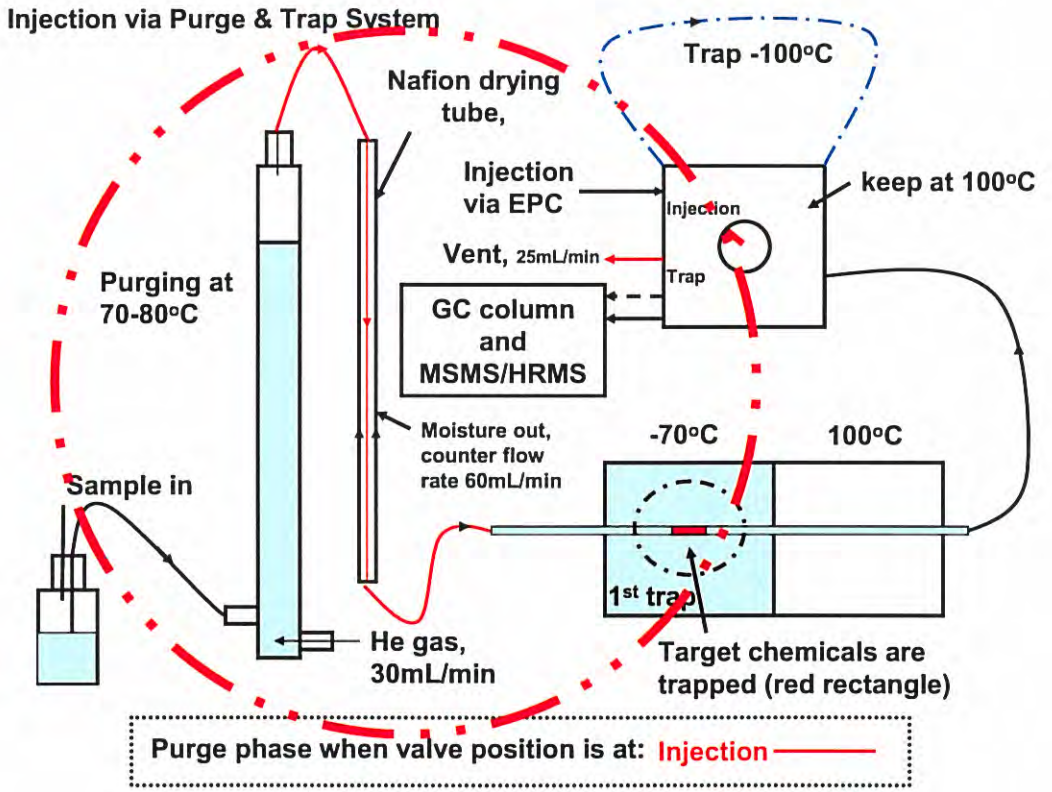


Injection of sample using purge and trap (P&T) system:

Injection of sample using purge and trap system consists of two phases, i.e. the purge and desorption phases.

During purging (Figure 2a), sample is introduced into the purger and it is purged by He at a flow rate 30ml/min at 70-80°C for 30min. During purging, the unibeads inside the glass rod should be at -60 - -70oC and the valve should be at injection position. The target chemicals will be trapped in the unibeads while the He gas will be released at the vent.

Figure 2a



At desorption phase, target chemicals will be released from the unibeads. Before desorption (Figure 2b), valve should be at trap position, and the unibeads will be pushed to 100°C. Target chemicals will be released at high temperature and will then be trapped at the second trap in liquid nitrogen. Wait for 3min and then turn the valve