

A Collection Method for Nonmethane Organic Compounds

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Abstract

Nonmethane organic compounds (NMOCs) that originate from both natural and anthropogenic sources act as precursors in the formation of oxidants in the troposphere. These NMOCs lead to the eventual production of ozone through a series of complex reactions with the hydroxyl radical and the oxides of nitrogen. A common sampling method involves the collection of whole air samples in passivated stainless steel canisters. The air samples can be (1) passively obtained in a pre-evacuated canister or (2) pressurized with ambient air via a pump. The objective of this study was to compare the two methods. The samples were analyzed through cryogenic preconcentration/high resolution gas chromatography with flame ionization detection. Measurements for 21 target analytes were compared with the precision of the analytical technique to determine any differences between the sampling methods. No real difference could be observed for approximately 13 out of the 21 analytes that were measured with good analytical precision. However, the technique for manual integration of the chromatographic peaks that are poorly resolved needs to be revised in order to evaluate the sampling methodologies for the complete list of 21 target analytes.

Introduction

Nonmethane organic compounds (NMOCs) consist of a complex mixture of chemical compounds containing between 2 and 12 carbon atoms. Present in the atmosphere at levels ranging from pptv to ppbv, several hundred milliliters of air must be pre-concentrated in order to detect the NMOCs. Typically, whole air samples are collected in passivated stainless steel canisters and are analyzed by cryogenic preconcentration/high resolution gas chromatography with flame ionization detection (FID). The samples can either be collected by passively controlling the flow of air into an evacuated canister with a critical orifice or by pumping a metered flow of air into an evacuated canister. Five one hour integrated samples were run simultaneously on each sampling technique. The difference between the concentrations of 21 target analytes measured by the sampling systems was compared with the precision of the analytical technique.

Experimental Design

- ◆ Sample Preparation
 - Canister Cleaning System
- ◆ Sample Collection
 - Passive, Critical Orifice Upstream, & Critical Orifice Downstream
- ◆ Sample Analysis
 - Cryogenic Preconcentration
 - Gas Chromatography with flame ionization detection (FID)

Sample Preparation: Coulter Counter Cleaning System

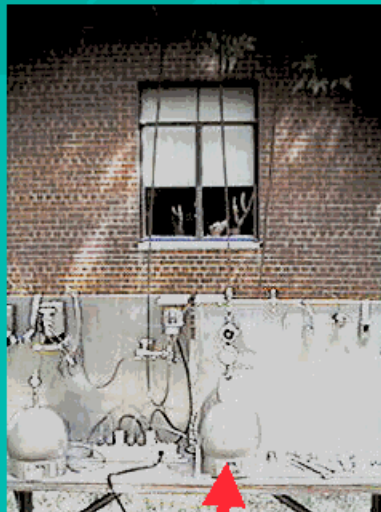


Sample Collection

Prior to sample collection, the passivated stainless steel canisters were brought to a final evacuation pressure of less than 30 mtorr using humidified ultra zero air and a stainless steel manifold that could accommodate 8 canisters. After this cleansing process, two different methods were used to collect the air samples. In the passive technique, a critical orifice was connected in series with a Wilson discharge flow controller to provide a constant air flow into the pre-evacuated canister. In the second technique, a Wilson discharge pump was used to evacuate the pre-evacuated canister with ambient air. In one approach of this sampling system, a critical orifice was connected upstream of the pump to meter the air flow into the canister while the other approach utilized a discharge flow controller downstream of the pump to provide a constant flow into the canister.

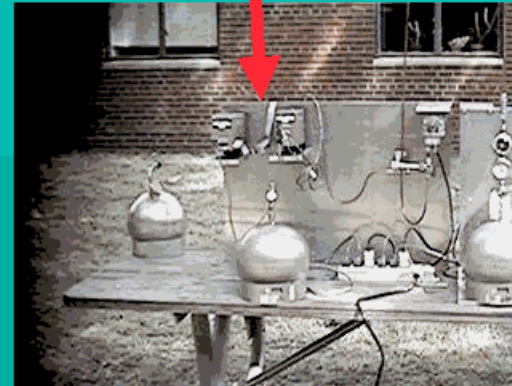
Sample Collection Site

Critical Orifice
Downstream



Passive

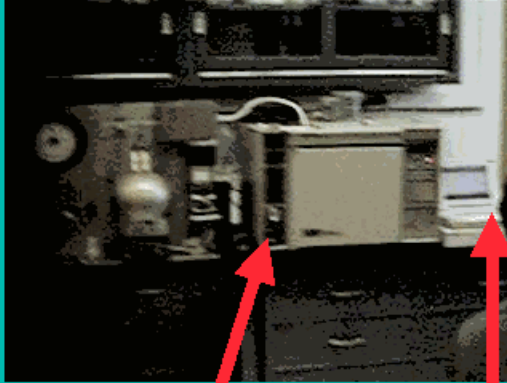
Critical Orifice
Upstream



Sample Analysis

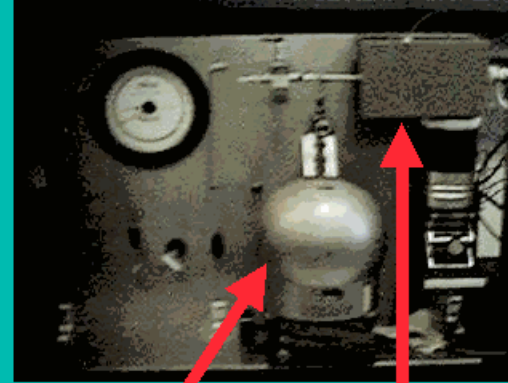
Following collection, the NMOCs in the whole air samples were preconcentrated by immersing a 9-cm x 0.180-cm-I.d. section of Silcosteel tubing packed with fused silica wool into liquid Argon (-180°C). Afterwards, the NMOCs were thermally desorbed by immersing the tubing into boiling water for 2 minutes. Following this process, the sample was transferred to (1) a 60-m X 0.32-mm-I.d. fused silica capillary column coated with a 1 micrometer thick film of polydimethylsiloxane for the analysis of C₃ to C₁₂ hydrocarbons and oxygenated hydrocarbons (OxHCs) and (2) a 30-m X 0.53-mm-I.d. porous layer open tubular column coated with alumina for analysis of the C₂ hydrocarbons. The FID was calibrated daily with a mixture of C₂ - C₆ n-alkanes, benzene, and toluene at a level of 10 ppbv each. Analytic precision of these standard compounds is approximately 3-4%. The detection limit of the technique is 10 pptC for a 500-ml sample volume.

Analytical System



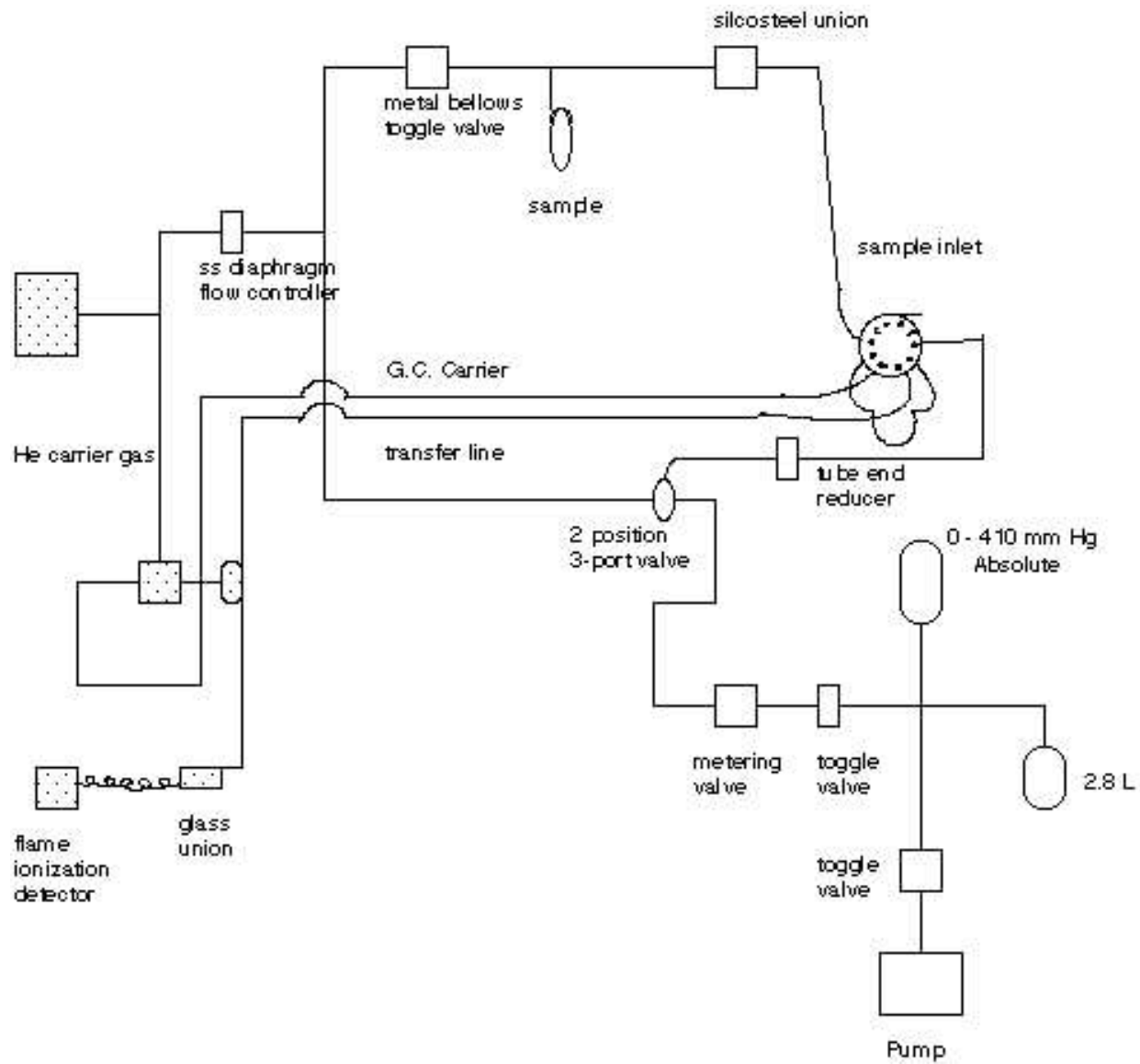
G.C. Alumina Column

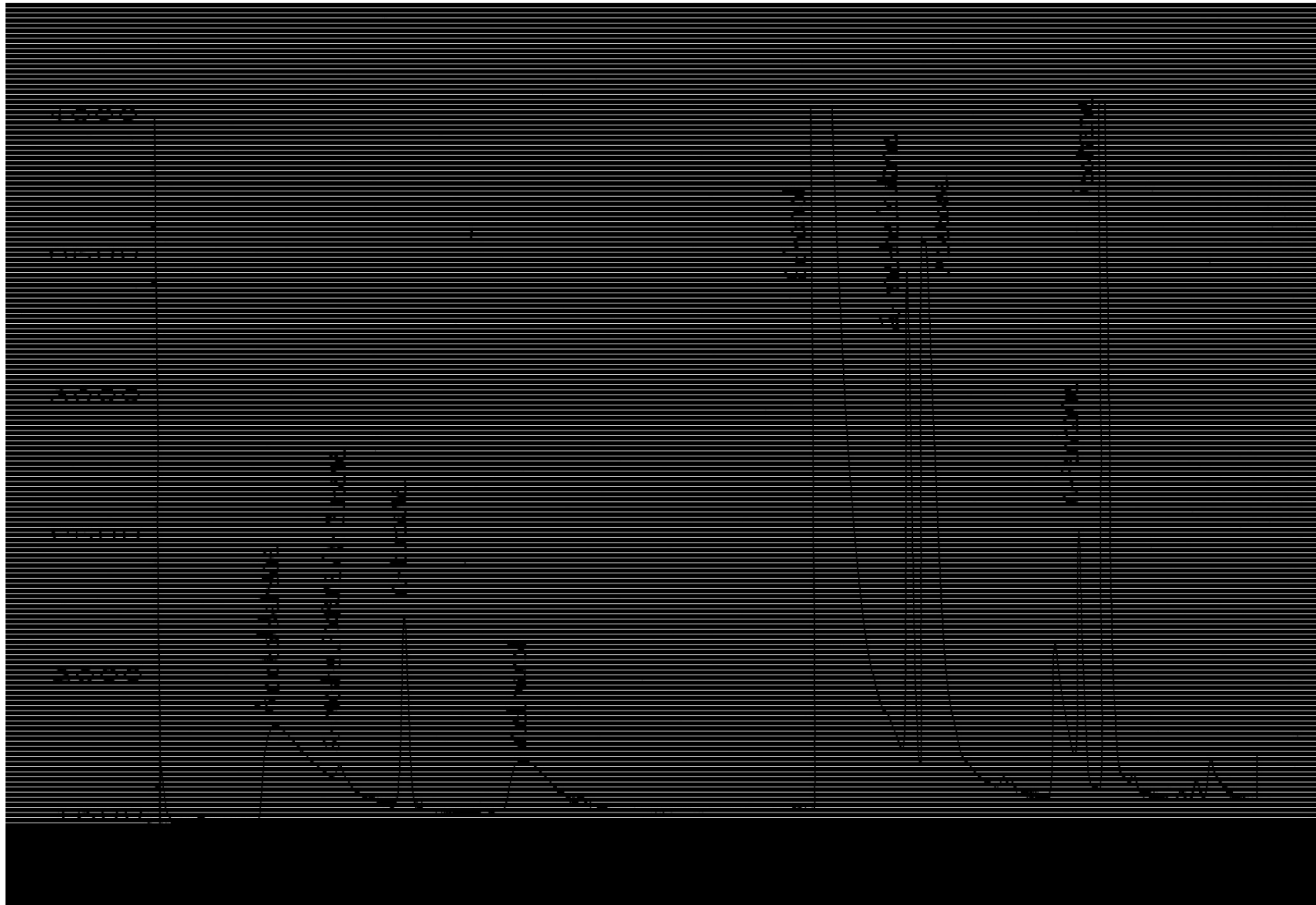
H.P. Analyzer



Sample Canister

Preconcentrator





Results

<i>Compound</i>	<i>Avg. Conc. ppbC</i>	<i>Precision of Analytical Inst. %</i>	<i>Passive % diff. avg</i>	<i>C.O. U-stream % diff. avg</i>	<i>C.O. D-stream % diff. avg</i>
1-propene	0.17	18.3	19.6	35.7	15.3
Propane	1.3	23.6	1.5	3.1	3.1
2-methylpropane	0.51	4.18	1.4	3.2	2.9
acetaldehyde	3.2	62.6	12.2	21.3	31.2
2-methylpropane	0.27	10.1	4.4	15.1	20.7
n-butane	1.3	1.62	1.6	0.6	0.6
methanol	2.8	41	4.3	28.6	36
ethanol	19.31	39.6	85.5	80.8	91.2
2-methylbutane	2.5	11.2	8.6	6.7	7.9
acetone	9.8	7.4	9.6	8.2	9.3
n-pentane	1.4	10.4	7.1	6.4	6.3
acetone	6.6	1.21	4.2	4.3	3.1
n-hexane	9.67	12.2	9.1	9.2	9.6
benzene	1.1	17.1	6.18	5.95	4.28
toluene	7.9	2.22	1.32	1.22	2.01
styrene	0.29	6.2	7.2	5.7	5.4
p-methylar	1.89	10.7	11.1	9.1	8.9
o-xylene	0.81	7.38	18.1	6.6	13.3
ethane	2.0	3.3	2.7	0.22	0.2
ethane	0.88	2.8	2.5	2.2	2.5
methylar	0.86	4.3	4.1	4.2	4.4

Discussion

No differences between the samplers could be determined for the poorly resolved analytes because of a lack of precision in the manual integration of the chromatograms. For example, the chromatographic results exhibited partial separation of analytes accompanied by peak tailing of the lower molecular weight oxygenated hydrocarbons (OxHCs). Partial separation could be seen in the highly volatile analytes that could not be retained on the column such as propane and propene. Peak tailing, demonstrated in acetaldehyde, was partially due to the presence of water in the sample. Water, with the ability to act as a stationary phase, affected the diffusivity of analytes on the column thereby degrading the resolution of the OxHCs. Both of these conditions (lack of separation and longitudinal diffusion) made it difficult to distinguish peaks, causing interference with proper integration and thus leading to high precisional variance for some analytes.

Other factors also contributed to the variance in precision. The smaller the concentration of analyte, the weaker the response, which in turn hindered detection. To elaborate, 2-methylpropene at a concentration of 0.27 ppbC had a high variance of 18.1%, while toluene at 2.2 ppbC had a lower variance of 2.2%. In addition, one consistent observation in the data was the high levels of ethanol found

Discussion continued

in the sampling system that positioned the critical orifice downstream of the pump. Such levels suggested either a high efficiency of, or possible contamination in, the pump or flow controller. Furthermore, one sampling method could have had more active sites available for one particular analyte than another. In general, higher quality chromatography induces better precision. Once satisfactory precision is obtained, the sampling techniques can be evaluated for the complete list of target analytes.

Conclusion

The variation in analytical precision was mainly due to partial separation of analytes, peak tailing, minimal analyte concentrations and the lack of ability in the manual integration technique. The main improvement needed is the development of a dual column technique coupled with column switching. For example, a polar column could retain water along with any OxHCs that may be present while at the same time allowing non-polar compounds to elute on the following column. In addition, the development of a consistent integration approach that accounts for peak tailing and other 'trouble spots' would further minimize other variations in the precision. With such improvements, differences between sampling methods can be fully characterized.

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