

**Interpretation and Data Quality Evaluation of Hourly Measurement of
Target VOCs by AutoGC/MS at the New Hendersonville, TN,
Southern Oxidants Study Site, June 17-27, 1995**

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INTRODUCTION

The North American Research Strategy for Tropospheric Ozone (NARSTO) program has sponsored the development and evaluation of monitoring methods for volatile organic compounds (VOCs) that are associated with the formation of tropospheric ozone. Target VOC lists have been developed that are designed to be reflective of the VOCs of concern in ozone formation. These lists are evolving as understanding of the processes develops.^{1,2} Our samples were analyzed for a target list that included 57 ozone precursor compounds, the 41-compound TO-14 list, and 10 selected aldehydes. Two field autoGC systems were deployed at the New Hendersonville, TN, site which was one of the intensive measurement sites for the 1995 Southern Oxidants Study (SOS). This site, approximately 15 mi northeast of Nashville, was selected to be a downwind site, although as data in a companion paper demonstrated,³ this was rarely the case for the June 17-27 period that we made measurements. In this paper, quality assurance issues related to the calibration, sampling integrity, and artifacts are discussed, and quantitative measures of data quality are described. Canister and sorbent tube samples were also taken concurrently with some of the hourly measurements, and the concurrent measurements are compared in this paper.

EXPERIMENTAL

Two autoGC/MS systems for monitoring VOCs in air were field tested. Both systems were housed in an environmentally controlled trailer and required no cryogenic liquids for sample collection or chromatographic separation.

Trailer

The outside dimensions of the mobile laboratory are 8.5 ft wide by 25.5 ft long, including the tongue, and the inside dimensions are 8 ft by 20 ft. The laboratory is furnished with two instrument benches, which measure 10 and 11 ft long, two gas bays that will accommodate a total of 8 cylinders, a computer desk, a storage closet, a small refrigerator, and storage shelves and drawers. Two heating/air conditioning units (20 A, 120 V) and two ceiling ventilation fans are available for temperature control. The laboratory is equipped with two 50-A 240-V electrical boxes and a total of 64 outlets. A telescoping meteorological tower which came with the trailer malfunctioned and was replaced with a demountable tower. Air was taken from the 30-m-high sampling manifold (erected by Georgia Institute of Technology) by heated transfer line into a distribution manifold that was inside the monitoring trailer.

XonTech/Saturn System

One autoGC system includes a prototype sample preconcentrator designed by XonTech, Inc. (Van Nuys, CA), that is based on the Stirling refrigeration cycle. This preconcentrator is interfaced to a Varian Saturn II GC/Ion Trap mass spectrometer (Walnut Creek, CA). The preconcentration system consists of two multisorbent traps (Tenax-GR/Carbotrap B/Carbosieve S-III) for sample collection at ambient temperatures. Once the air sample has been concentrated on the trap, the sample is desorbed onto a second (unpacked) trap which has been cooled to $-165\text{ }^{\circ}\text{C}$ by the Stirling closed-cycle cooler. The sample is effectively focused on this second trap so that upon desorption at $100\text{ }^{\circ}\text{C}$ to the GC column, the analytes are well separated without using subambient GC oven temperature programming. After separation on the Varian Star 3400 GC column, the analytes are detected with the Saturn ion trap detector. The system has been evaluated with the TO-14

compound mixture, a polar VOC mixture, and the ozone precursor mixture. Excellent results have been achieved with regard to trapping efficiency and linearity of response.⁴

Perkin Elmer ATD 400/Q-Mass 910 System

The second benchtop GC/MS system to be evaluated was made available to EPA by the Perkin Elmer corporation (Norwalk, CT) and it includes an ATD 400 Auto Thermal Desorption system, an Autosystem gas chromatograph, and a Q-Mass 910 mass spectrometer. The ATD 400 is the sample concentration and desorption device for the system, and it incorporates a multisorbent packed cold trap that is cooled by a Peltier cooler. The ATD 400 is connected to the Autosystem GC through a heated transfer line that is connected within the GC oven to a high-capacity, fused-silica capillary column (50 m × 0.32 mm × 5.0 μm dimethyl polysiloxane). The GC column is connected to the Q-Mass 910 quadrupole mass selective detector through a direct interface. The overall design of this system makes it feasible to collect and analyze VOCs without the requirement for a cryogen, such as liquid nitrogen. This system was evaluated in two ways to determine its performance in VOC sample analysis using a sorbent tube sampling method.

1. Perkin Elmer sorbent tube collection—sorbent tube used to collect sample from the manifold or directly in an outdoor setting is desorbed on ATD 400 by using the cold trap for concentration
2. Summa-polished canister collection—sample transferred from canister onto a sorbent tube for subsequent analysis using ATD 400 cold trap for concentration

RESULTS AND DISCUSSION

Quality Assurance Project Plan

Before we went to the field, a Quality Assurance Project Plan was written and approved by appropriate ManTech and EPA QA and management personnel. In the plan, we set out our objectives for the study, schedules, responsibilities of each staff member, and our overall study design, meeting all criteria for a Class III Project.⁵ The approximate overall goal for each quantitative QA objective is given in the following tabulation. Specific target objectives were set for each compound, based on the previous performance history of each compound on each analytical system.

QA Objectives	XonTech		ATD 400/Q-Mass	
	Saturn	Manifold	Canisters	Sorbent Tube
Method Detection Limit	0.1 ppbv	0.5 ppbv	0.5 ppbv	0.5 ppbv
Relative Percent Difference	10%	25%	25%	25%
Internal Audit Accuracy	20%	30%	30%	N/A
Completeness	75%	75%	75%	75%

Target Compounds

The target lists of compounds for which we calibrated the GC/MS systems are given in Table 1. We made a concerted effort to coordinate with other NARSTO and SOS researchers to seek common target lists as much as we could. Although we understood that the standard target list of the Photochemical Assessment Monitoring Station (PAMS) program was undergoing reevaluation, we used the Alphagaz Ozone Precursor 57-compound standard, as we had it available and all systems had been characterized with this standard. We calibrated for the TO-14 target list because of our long history of using this standard and because we could use it as a benchmark for quick field evaluation of system performance. Because of the expressed interest in oxygenated compounds, we

added an aldehyde/ketone standard to our target list. It was prepared by injecting 100 μL of dilute aqueous solution of selected aldehydes and ketones into an evacuated canister and was used as a semiquantitative calibration standard. Storage stability was only marginally evaluated because of the press of time in preparing for the study. The limited evaluation showed that the very volatile and the heavier compounds both demonstrated low recoveries. Further work is required to develop methods for the preparation of adequate quantitative standards for these compounds.

Audit Standard Analysis

We conducted a blind analysis on both GC/MS systems. The audit canister was shipped to the field site by the NERL Quality Assurance Branch. The results of these analyses are given in Table 2. The QA laboratory analyzed the canister, using a Nutech preconcentrator with Nafion dryer. The canister had been filled from a high-pressure cylinder containing one of the series of audit standards used in the PAMS program. As a measure of precision, we computed the percent relative difference between replicate analyses on each system. Excellent internal precision was found for all measurements. After all results were validated and reported, the field analysis results were compared to the QA lab results. Both the XonTech Saturn and Perkin Elmer results were within acceptable limits and better than the QA lab analysis results, except for the instance where the Perkin Elmer missed the identification of 2,3-dimethylbutane.

GC Retention Time Stability

Retention time stability is a critical issue in measuring ozone precursor compounds, as similarity in mass spectra of the prevalent hydrocarbon compounds may cause inaccurate identification of the VOCs. Operating two heat-generating GC/MS systems in a trailer in the summer raises the question of GC retention time drift with variations in the trailer temperature. We suffered periodic air conditioner freeze-up during our 10-day study. This resulted in only one delayed start of the GC, as the trailer ambient temperature was near the GC start temperature. We were particularly concerned about retention time stability in the operation of our system, because we employ absolute rather than relative retention times in our identification. Despite these worries, the retention time stability of both systems was excellent, as illustrated in Figure 1.

Data Capture

Hourly measurements were taken continuously from June 17 through 27, with the only time lost for daily calibration checks and two power interruptions during the course of the study; samples were taken for 191 hours out of a scheduled 200. This represents 95% data capture for the XonTech/Saturn system. The Perkin Elmer system was not operated in a continuous mode, so calculation of completeness does not easily apply. The Perkin Elmer did demonstrate a greater sensitivity to humidity as samples taken during rain events and in the early morning showed depressed response because of the condensation of liquid water in the sampling tube and the previously demonstrated limited pumping capacity of the Q-Mass mass spectrometer.

Potential Manifold and Transfer Line Artifacts

Prior to the study, concern was raised by study participants about the length of the sampling manifold (30 m) and the successful transfer from the manifold into our sampling van. This concern was raised because of the anticipated "stickiness" of some of the heavier (C_8 - C_{10}) aldehydes. A cross-linked FEP/PTFE Teflon-coated manifold was especially constructed by University Research Glass (Carrboro, NC) for the Georgia Tech researchers. We procured a 40-ft heated PFA Teflon transfer line (Unique Products, Inc., Hazel Park, MI) and tested it prior to installation. The line

was purged with humidified scientific-grade air and the output analyzed; no artifacts were seen above background. We also challenged the line with standard gas from our calibration manifold; no compounds showed diminished response from passing through the transfer line. Additional testing for artifacts has continued since June.

CONCLUSIONS

Trailer-based near-real-time measurements of VOCs related to ozone formation can be made with high and measurable data quality. Reasonable accuracy and excellent precision were demonstrated. Greater than 95% data capture was achieved for the 10-day study.

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Table 1. Target Compounds for Nashville 1995 Summer Study.

Ozone Precursors (Alphagaz Standard)

Isobutane
 1-Butene
n-Butane
trans-2-Butene
cis-2-Butene
 3-Methyl-1-butene
 Isopentane
 1-Pentene
n-Pentane
 Isoprene
trans-2-Pentene
cis-2-Pentene
 2-Methyl-2-butene
 2,2-Dimethylbutane
 Cyclopentene
 4-Methyl-1-pentene
 2,3-Dimethylbutane
 Cyclopentane
 2-Methylpentane
 3-Methylpentane
 2-Methyl-1-pentene
n-Hexane
trans-2-Hexene
cis-2-Hexene
 2-4-Dimethylpentane
 Methylcyclopentane
 Benzene
 Cyclohexane
 2-Methylhexane
 2,3-Dimethylpentane
 3-Methylhexane
 2,2,4-Trimethylpentane
n-Heptane
 Methylcyclohexane
 2,3,4-Trimethylpentane
 Toluene
 2-Methylheptane
 3-Methylheptane
n-Octane
 Ethylbenzene
m,p-Xylene

Styrene
o-Xylene
n-Nonane
 Isopropylbenzene
 α -Pinene
n-Propylbenzene
 1,3,5-Trimethylbenzene
n-Decane
 β -Pinene
 1,2,4-Trimethylbenzene
 Undecane

TO-14 Standard (Alphagaz)

Dichlorodifluoromethane
 Chloromethane
 1,2-Dichloro-1,1,2,2-tetrafluoroethane
 Chloroethene
 Bromomethane
 Chloroethane
 Trichlorofluoromethane
 1,1-Dichloroethene
 Dichloromethane
 3-Chloropropene
 1,1,2-Trichloro-1,2,2-trifluoroethane
 1,1-Dichloroethane
cis-1,2-Dichloroethene
 Trichloromethane
 1,2-Dichloroethane
 1,1,1-Trichloroethane
 Benzene
 Carbon tetrachloride
 1,2-Dichloropropane
 Trichloroethene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
 1,1,2-Trichloroethane
 Toluene
 1,2-Dibromoethane
 Tetrachloroethene
 Chlorobenzene
 Ethylbenzene
m,p-Xylene
 Styrene
 1,1,2,2-Tetrachloroethane
o-Xylene
 4-Ethyltoluene
 1,3,5-Trimethylbenzene
 1,2,4-Trimethylbenzene
 Benzyl Chloride
m-Dichlorobenzene
p-Dichlorobenzene
o-Dichlorobenzene
 1,2,4-Trichlorobenzene
 Hexachlorobutadiene

"Aldehyde Standard"

Methacrolein
 Methyl vinyl ketone
 Butanal
 1,1,1-Trichloroethane
 2-Pentanone
 Pentanal
 Trichloroethene
 Hexanal
 Tetrachloroethene
 Heptanal
 Benzaldehyde
 Octanal
 Nonanal
 Decanal

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Table 2. Precision and Accuracy of Analysis of Field Audit Canister 01628.*

Compound	Analysis Results		Replicate Average		Precision (%)**		Accuracy (%)***		
	QA Standard Target	Lab Found	X/S Found	PE Found	X/S	PE	QA Lab	X/S	PE
1-Butene	8.90	10.50	9.34	5.01	2.68	-41.79	117	104	56
<i>trans</i> -2-Butene	8.75	10.30	9.94	11.43	1.11	-1.50	117	113	130
3-Methyl-1-butene	11.00	13.10	9.10	10.38	-0.55	-3.32	119	82	94
1-Pentene	10.25	11.50	10.75	11.00	0.70	-6.00	112	104	107
Isoprene	9.55	12.00	8.55	9.84	1.75	-2.59	125	89	103
<i>cis</i> -2-Pentene	9.80	11.50	10.28	12.78	-0.12	2.03	117	104	130
2,2-Dimethylbutane	14.45	17.90	14.85	17.44	0.10	-2.16	123	102	120
4-Methyl-1-pentene	13.05	14.90	13.77	15.63	-1.20	1.77	114	105	119
2,3-Dimethylbutane	13.85	16.20	14.82	0.00	1.82	ERR	116	107	0
3-Methylpentane	14.05	16.60	14.94	15.46	0.00	-1.19	118	106	110
<i>n</i> -Hexane	13.85	15.50	14.94	15.91	0.60	1.19	111	107	114
<i>cis</i> -2-Hexene	13.10	14.70	14.13	15.40	0.74	-2.24	112	107	117
∞ 2,4-Dimethylpentane	16.75	18.20	16.52	17.94	0.64	0.47	108	98	107
Cyclohexane	14.45	16.70	15.96	14.14	1.32	0.62	115	110	97
2,3-Dimethylpentane	17.40	20.30	18.34	20.05	0.76	0.33	116	105	115
2,2,4-Trimethylpentane	20.30	23.50	20.84	22.69	0.10	-0.46	115	102	111
Methylcyclohexane	18.80	20.20	19.01	20.35	-0.09	2.17	107	101	108
2,3,4-Trimethylpentane	18.80	21.50	20.12	20.13	1.89	-0.93	114	107	107
2-Methylheptane	19.95	22.80	21.68	23.57	1.29	-0.86	114	108	118
Ethylbenzene	18.65	17.80	17.36	17.34	2.30	0.27	95	93	92
<i>m,p</i> -Xylene	18.70	17.80	17.60	16.75	3.64	0.53	95	94	89
<i>o</i> -Xylene	18.15	18.50	18.16	17.97	1.98	-0.06	101	100	99
Isopropylbenzene	19.95	20.50	20.16	20.27	1.56	0.55	102	101	101
1,3,5-Trimethylbenzene	18.75	19.20	20.30	18.34	2.99	0.09	102	108	97

*Abbreviations: X/S = XonTech Saturn, PE = Perkin Elmer. **Precision = $(a - b) \times 2 / (a + b)$. ***Accuracy = $\text{Found} \times 100\% / \text{True}$.

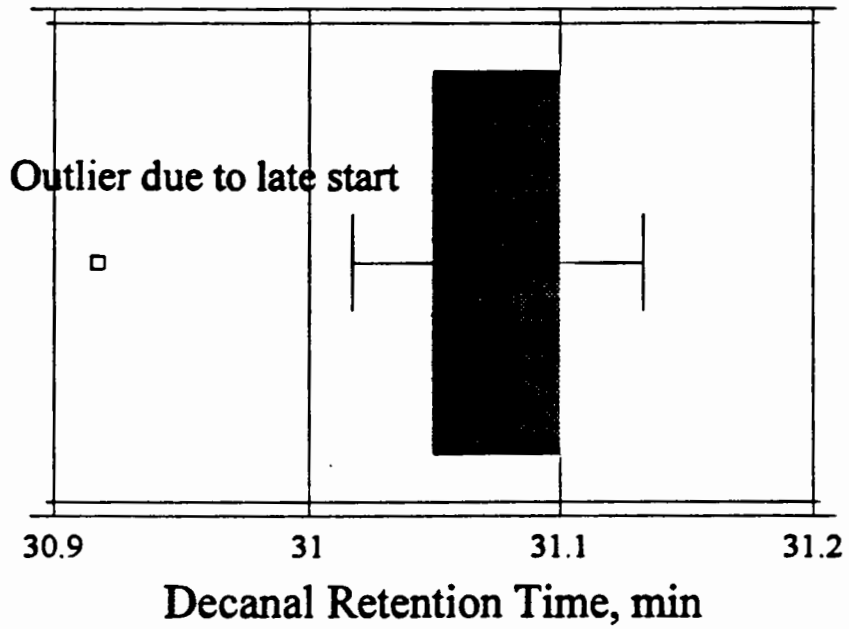


Figure 1. Typical Retention Time Stability for 10-Day Study.

TECHNICAL REPORT DATA

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