

## Journal of the Air & Waste Management Association

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/uawm20>

### Hydrocarbon Measurements During the 1992 Southern Oxidants Study Atlanta Intensive: Protocol and Quality Assurance

Eric C. Apel <sup>a</sup>, Jack G. Calvert <sup>a</sup>, Rod Zika <sup>b</sup>, Michael O. Rodgers <sup>c</sup>, Viney P. Aneja <sup>d</sup>, James F. Meagher <sup>e</sup> & William A. Lonneman <sup>f</sup>

<sup>a</sup> National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, Colorado, USA

<sup>b</sup> Rosenstiel School for Marine and Atmospheric Science, University of Miami, Miami, Florida, USA

<sup>c</sup> Georgia Institute of Technology, School of Earth and Atmospheric Sciences, Atlanta, Georgia, USA

<sup>d</sup> Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, North Carolina, USA

<sup>e</sup> Tennessee Valley Authority, Atmospheric Sciences Department, Muscle Shoals, Alabama, USA

<sup>f</sup> U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, USA

Published online: 05 Mar 2012.

To cite this article: Eric C. Apel, Jack G. Calvert, Rod Zika, Michael O. Rodgers, Viney P. Aneja, James F. Meagher & William A. Lonneman (1995) Hydrocarbon Measurements During the 1992 Southern Oxidants Study Atlanta Intensive: Protocol and Quality Assurance, Journal of the Air & Waste Management Association, 45:7, 521-528, DOI: [10.1080/10473289.1995.10467383](https://doi.org/10.1080/10473289.1995.10467383)

To link to this article: <http://dx.doi.org/10.1080/10473289.1995.10467383>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

# Hydrocarbon Measurements During the 1992 Southern Oxidants Study Atlanta Intensive: Protocol and Quality Assurance

**Eric C. Apel and Jack G. Calvert**

*National Center for Atmospheric Research, Atmospheric Chemistry Division, Boulder, Colorado*

**Rod Zika**

*University of Miami, Rosenstiel School for Marine and Atmospheric Science, Miami, Florida*

**Michael O. Rodgers**

*Georgia Institute of Technology, School of Earth and Atmospheric Sciences, Atlanta, Georgia*

**Viney P. Aneja**

*North Carolina State University, Department of Marine, Earth and Atmospheric Sciences, Raleigh, North Carolina*

**James F. Meagher**

*Tennessee Valley Authority, Atmospheric Sciences Department, Muscle Shoals, Alabama*

**William A. Lonneman**

*U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina*

## ABSTRACT

A major component of the Southern Oxidants Study (SOS) 1992 Atlanta Intensive was the measurement of atmospheric nonmethane hydrocarbons. Ambient air samples were collected and analyzed by a network of strategically located automated gas chromatography (GC) systems (field systems). In addition, an extensive canister sampling network was deployed. Combined, more than 3000 chromatograms were

recorded. The SOS science team targeted for quantitative analysis 56 compounds which may be substantial contributors to ozone formation or used as air mass tracers. A quality assurance program was instituted to ensure that good measurements were being made throughout the network for each target compound. Common, high-quality standards were used throughout the network. The performance of individual field systems was evaluated during the intensive through the analysis of challenge mixtures. This methodology helped to identify and correct analytical problems as they arose.

## IMPLICATIONS

Accurate measurements of ozone precursors are required to understand the process and extent of ozone formation in rural and urban areas. Nonmethane hydrocarbons (NMHCs) have been identified as important ozone precursors. Recently, automated gas chromatographic (GC) systems have been developed for both intensive field measurements and continuous monitoring of these species. Identification and quantification of NMHCs is difficult because of the large number present and the wide molecular weight range encountered in typical air samples. This article describes the efforts of a group of scientists to make high-quality automated GC measurements of targeted NMHCs during the Southern Oxidants Study (SOS) 1992 Atlanta Intensive. This work indicates the importance of proper gas standards, a well-thought-out protocol, and periodic evaluations of deployed measurement systems.

## INTRODUCTION

Automated gas chromatographic (GC) systems were deployed during the Southern Oxidants Study (SOS) 1992 Atlanta Intensive to measure a select group of nonmethane hydrocarbons (NMHCs). Table 1 lists the targeted priority compounds, which were chosen by the SOS science team after consideration of the following issues.

One of the most important criteria used to select compounds for analysis during the SOS study is the effectiveness of the compound in question in forming ozone. Various methods are available for ranking the species in this regard. One involves the use of concentration times HO-radical rate constant rankings. Another involves the similar adjustment of each species to "propene equivalents."<sup>1</sup> A third method often employed today is the use of Carter

**Table 1.** Target compounds for the Atlanta Intensive.

Ethylene	2,4-Dimethylpentane
Acetylene	1,1,1-Trichloroethane
Ethane	Benzene
Propylene	Cyclohexane
Propane	2,3-Dimethylpentane
Isobutane	Trichloroethylene
1-Butene	Methylcyclohexane
Isobutene	2,3,4-Trimethylpentane
n-Butane	Toluene
trans-2-Butene	n-Octane
cis-2-Butene	Perchloroethylene
3-Methyl-1-Butene	Ethylbenzene
Isopentane	m-Xylene
1-Pentene	p-Xylene
2-Methyl-1-Butene	Styrene
n-Pentane	o-Xylene
Isoprene	Isopropylbenzene
Trans-2-Pentene	$\alpha$ -Pinene
cis-2-Pentene	n-Propylbenzene
2-Methyl-2-Butene	3-Ethyltoluene
4-Methyl-1-Pentene	4-Ethyltoluene
3-Methyl-1-Pentene	1,3,5-Trimethylbenzene
Cyclopentane	2-Ethyltoluene
2-Methylpentane	$\beta$ -Pinene
3-Methylpentane	1,2,4-Trimethylbenzene
n-Hexane	d-Limonene
cis-3-Hexene	1,3-Diethylbenzene
Methylcyclopentane	n-Butylbenzene

maximum incremental reactivity factors,<sup>2,3</sup> which estimate ozone production from each individual compound in an emission data base. Consideration was given to which of these potentially important compounds was likely to be found in and around the Atlanta area. Recent data were used from several sources, including the Auto/Oil Air Quality Improvement Program.<sup>4</sup> Also used was the U.S. Environmental Protection Agency (EPA) 1990 study of hydrocarbons in the Atlanta area<sup>5-7</sup> and the Alabama ROSE study.<sup>8</sup> Additional important input to the hydrocarbon priority list was that from the photochemical ozone modelers in the program. They felt that certain less reactive hydrocarbons, as well as the most reactive precursors to ozone formation, would be valuable in characterizing the origin of air masses and in tests for consistency in analysis.

A series of tests was planned and conducted to evaluate the analytical capabilities of the participant laboratories scheduled to make measurements during the 1992 Atlanta Intensive. Initial challenge tests were organized and carried out by the Hydrocarbon Measurements Technology and Standards (HCMTS) group of the SOS. The HCMTS group was formed specifically to supply standards, test each participant's measurement capabilities, and provide a measure of quality control and assurance. The HCMTS group was closely aligned with and run by the same group at the National Center for Atmospheric Research (NCAR) as the International Non-Methane Hydrocarbon Intercomparison

(NOMHICE), sponsored by the National Oceanic and Atmospheric Administration (NOAA).

Concomitant with the series of tests previously described and prior to the Atlanta Intensive, research was performed by participating scientists to address fundamental questions, such as the assumed equal per carbon response of the flame ionization detector (FID) for nonmethane hydrocarbons. Specific analytical challenges were also addressed, such as improving retention time reproducibility and reducing potential problems associated with canister sampling. A sampling of this research is described in this paper.

During the Atlanta Intensive, analysis laboratories were placed at three sites referred to here as Sites 1 (Lost Mountain), 2 (Georgia Institute of Technology), and 3 (South DeKalb). Additionally there were six canister sampling sites. The location of these sites is described elsewhere.<sup>9</sup> At all sites, continuous analyses were performed, and the samples collected at the canister sampling sites were analyzed at Sites 1 and 2. Common high-quality standards were deployed at each analysis site and run every day. These included the gravimetric standard for calibration of the GC system, an internal standard containing four compounds used as retention time markers, and a 56-component standard, containing all of the target compounds. This latter standard was provided to help ensure that the GC systems properly identified all of the target compounds. A methodology was set up to evaluate whether the analytical systems were functioning properly during the intensive. This was accomplished through the distribution and subsequent evaluation of challenge mixtures by the site scientists.

## EXPERIMENTAL METHODS EMPLOYED PRIOR TO THE ATLANTA INTENSIVE

A series of tests was devised to help evaluate the performance of the systems being used by the scientists who would eventually make measurements during the Atlanta Intensive. These tests consisted of distributing to the participants sample mixtures containing relevant hydrocarbons. The participants were asked to analyze these mixtures and to report their findings to NCAR-HCMTS.

## EXPERIMENTAL TECHNIQUES

Before distribution to participants, the mixtures were analyzed by NCAR-HCMTS using established techniques.<sup>10,11</sup> The gas chromatographs were Hewlett-Packard Models HP5880 and HP5890. The analytical columns were J&W Scientific DB-1 30-meter (1- and 3-micron film thickness) and DB-1 100-meter (0.5-micron film thickness), and a 20' x 0.030" I.D. packed column (phenyl isocyanate stationary phase).<sup>10</sup> The packed column separated C<sub>2</sub> through C<sub>4</sub> compounds with good resolution. Standard sample amounts ranged from 200 to 500 cm<sup>3</sup> (at STP). Samples were preconcentrated in a 60-80 mesh stainless steel loop filled with glass beads and immersed in liquid argon. Trapped samples were desorbed for

1.5 min at approximately 90 °C. The total volume sampled was determined by measuring the pressure difference in a previously evacuated known fixed reservoir using a pressure transducer (MKS Model 127AA). For experiments utilizing the DB-1 column, the analytes were refocused at the head of the column at -50 °C. The column temperature program was an initial hold for two min at -50 °C, followed by a temperature ramp from 50 to 150 °C at 4 °C/min. Integration of sample chromatograms was performed by HP Chemstation software for the HP5890 chromatograph and system software for the HP5880 chromatograph.

The mixtures were also analyzed by the EPA Atmospheric Research and Exposure Assessment Laboratory (AREAL/EPA), Research Triangle Park, NC, and these results and the NCAR-HCMTS results were compared and checked for consistency.

Mixtures were transferred quantitatively to NCAR-made, humidified,<sup>10</sup> electropolished stainless steel canisters. The samples were first analyzed by NCAR-HCMTS to ensure integrity and then shipped to participating laboratories. The participant laboratories were asked to perform canister analyses as quickly as possible using their existing techniques and then to return the canister with a sufficient amount of sample to permit reanalysis at NCAR. The reanalysis was done to determine sample integrity over the time of the experiment.

## PRELIMINARY TESTS AND RESULTS

### Test 1

The objective of this first test was to evaluate the quantitative accuracy of the participant laboratories through the analysis of a simple two-component standard mixture. The test results provided insight into the efficacy of the analytical methods used, particularly the gas standard employed. HCMTS ordered and obtained standard mixtures from the National Institutes of Standards and Technology (NIST) in five separate cylinders. Each cylinder had a slightly different concentration from the others. This initial mixture contained only n-butane and benzene at near-10-ppbv levels. NIST prepared the standards via the microgravimetric technique followed by dilution to obtain the final concentrations (ppb mole/mole). The uncertainty in the NIST results<sup>12</sup> was determined by summing in quadrature: (a) the preparation uncertainty of gravimetric standards, (b) the uncertainty in intercomparing the mixture with other gravimetric standards, and (c) the uncertainty in replicate determinations from various days. Hence, the total uncertainty for each compound concentration reported by NIST was determined by the expression  $2(a^2 + b^2 + c^2)^{1/2}$ . The total uncertainty varied only slightly from cylinder to cylinder and was  $\pm 2\%$  for benzene and  $\pm 3\%$  for n-butane (both expressed at the 95% confidence limit).

Samples were analyzed by NCAR-HCMTS and sent to participating laboratories. These included groups from Georgia Institute of Technology (GIT), Tennessee Valley Authority (TVA), North Carolina State University (NCSCU), NCAR, NOAA,

and the University of Miami/Rosenstiel School of Marine and Atmospheric Science (RSMAS). The laboratories performed their analyses and returned the samples to NCAR-HCMTS for reanalysis. In some cases, significant discrepancies from the NIST values were found. The percentage difference from NIST ranged from +8 to -29% for butane, and +7 and -28% for benzene.

When large discrepancies were observed with a participant laboratory, the standards employed for calibration by individual laboratories were sent to the NCAR-HCMTS laboratory and crosschecked against standards obtained from NIST, National Physical Laboratory (NPL), and Environment Canada Laboratory. NCAR-HCMTS was able to provide useful feedback to participants on the differences observed among the standards. The decision was made thereafter for all participants to use gravimetric standards derived from a common source (NIST) and crosschecked against each other to ensure consistency.

### Test 2

Samples containing a 62-component mixture of hydrocarbons (and halocarbons), prepared by the AREAL/EPA Laboratory, were sent to participants (which were the same as in Test 1, except that the Oregon Graduate Institute [OGI] replaced NOAA) prior to an informal workshop held at RSMAS. Each participant analyzed the mixture several times to obtain statistics on both the retention time reproducibility and the absolute concentrations of each component. In addition to quantitative intercomparison among groups, the mixture was used to help select the best GC column for maximum component resolution.

The general conclusions from this study were as follows:

1. The NIST standard of butane and benzene (approximately 10 ppbv) supplied to all future SOS Atlanta Intensive participants (GIT, NCSU, and RSMAS) enabled these laboratories to calibrate their respective instruments effectively and without potential bias from improperly prepared standards.
2. The analysis of C<sub>2</sub> hydrocarbons could be done on a single column (100-m DB-1) along with all other hydrocarbons in the mixture under the proper conditions as demonstrated by the RSMAS group, using a preconcentration device purchased from Entech Laboratory Automation (Model ELA 2000).
3. The analysis of biogenic hydrocarbons, isoprene, and  $\alpha$ -pinene, especially important for the SOS program, was conducted well by all groups. The  $\beta$ -pinene posed a much greater challenge. The concentration of  $\beta$ -pinene decreased with time in the canisters and, concomitant with this decrease, two new products appeared. It was difficult to ascertain whether this occurred because of problems with storage of this compound, or with problems associated with introducing it into the analytical system, or both.

4. The participants' ability to reliably reproduce retention times for the various hydrocarbons varied from one group to another. Repetitive retention times by the automated and semi-automated GC systems were considered essential for correct compound peak identification.

### Test 3

The GIT, TVA, NCSU, and RSMAS groups participated in an SOS hydrocarbon workshop hosted by RSMAS. The major experiment conducted at the workshop involved studies of a prepared cylinder (Scott Specialty Gases) containing all of the 56 targeted priority compounds. The mixture was used to develop positive identification strategies for the priority compounds. Two brands of automated preconcentration devices were represented: Chrompack (CP 9000) and Entech (ELA 2000). A semi-automated system was also represented.<sup>13</sup> Although all systems operated satisfactorily, it was decided that the selection of one system for the 1992 Atlanta Intensive study would provide consistency to the field operation program. The Entech preconcentration system was selected for the Atlanta Intensive study based upon several perceived advantages, including user friendliness and system reliability, and the system's ability to meet the following basic requirements: (1) the ability to resolve the C<sub>2</sub> compounds on the same column as the other 53 compounds, (2) the capability to inject an internal standard during each run to correct for drift in retention time windows, and (3) the need to leave the unattended system operating for hours at a time. A complete description of the system as it was deployed during the study is given by Farmer et al.<sup>14</sup>

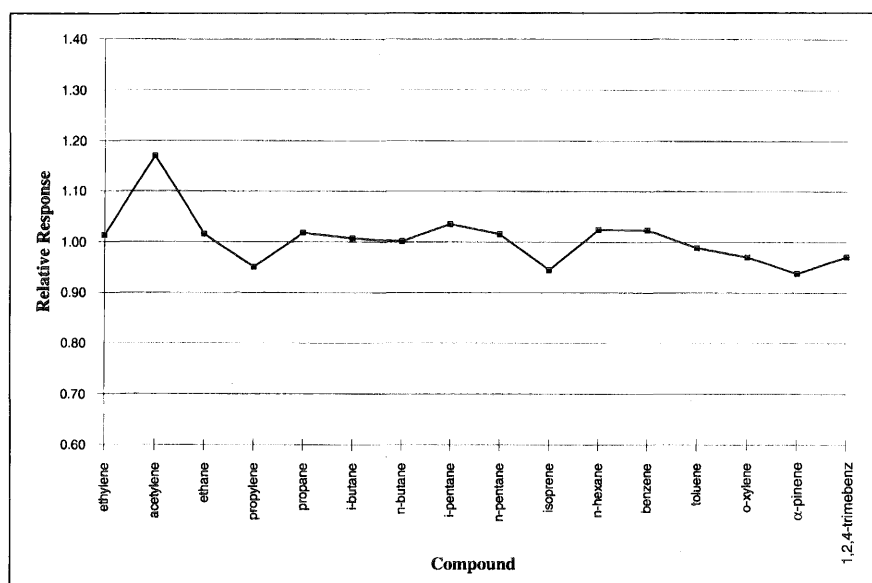
### RESEARCH CONDUCTED PRIOR TO THE ATLANTA INTENSIVE

Preliminary research was conducted to address specific issues that had a direct bearing on the quality of measurements and reliability of data. One basic issue concerned the FID response factors of individual nonmethane hydrocarbons of the 56-component priority group. Another issue discussed previously was retention time variability between runs on the GC system. A large component of the measurement strategy involved the collection of air samples in canisters deployed at strategic locations. This activity raised several questions regarding potential problems involved in canister sampling, storage, cleaning, and handling.

Reports in the literature indicate

that the FID response for hydrocarbons is generally proportional to the mass of carbon present in the sample,<sup>15-17</sup> at least throughout a given range of compounds studied. The exception to this for previously studied compounds is acetylene, which has an anomalously high response.<sup>17</sup> To further investigate the assumption of equal per carbon response, NCAR-HCMTS ran a series of experiments with an NIST-prepared, 16-component, gravimetric standard and compared the relative per carbon response for each compound. Figure 1 is a plot of the relative response per carbon number, with respect to n-butane, for the 16 compounds in the NIST standard. The sample was taken directly from the cylinder to avoid any possible canister effects. The values given represent an average of two measurements. The precision of the NCAR-HCMTS measurements is  $\leq \pm 2\%$ , and the uncertainty of the NIST standards is  $\leq \pm 3\%$ . The result for acetylene is anomalous, compared to the other compounds in the mixture. For the remaining compounds, the largest deviation from 1.00 is 6%. As a crosscheck on NIST materials, gravimetric standards supplied by NPL and Environment Canada Conservation and Protection Laboratory were compared to the NIST mixtures. Preliminary results indicate that the agreement among the three laboratories is, for many compounds, within  $\pm 10\%$ . Thus, although reliable gravimetric standards were not available for all of the target compounds, these results generally indicate that the concentrations of target hydrocarbons could be approximated reasonably well ( $\pm 6\%$ , compared to n-butane) by assuming equal per carbon FID response.

The retention time variability was corrected by taking advantage of the Entech preconcentrator's ability to simultaneously inject internal standards with every run. Research was conducted to determine the best possible compounds



**Figure 1.** Relative response of the FID detector versus compound for an NIST 16-component gravimetrically prepared standard. An HP5890 Series II GC was used with a DB-1 100-m, 0.5-micron film thickness column installed.

to be used for the range of hydrocarbons measured.<sup>14</sup> Four compounds were chosen: 1,1-difluoroethylene, 2,2-dimethyl butane, 3-fluorotoluene, and n-decane. The concentrations were not critical because the volume of the internal standard introduced could be controlled. The software (HP Chemstation) was set up to flag these compounds as reference materials and to adjust the retention time windows accordingly for each run for each priority compound.

A large effort was put into designing, testing, and selecting the canister sampling network, but this will not be discussed in depth here. Protocols were developed for canister sampling, cleaning, and handling, based on the expertise of the research groups involved. The turnaround time for canisters was scheduled to always be less than two weeks to minimize sample storage times. Stability of air samples over this time period was not thought to be a problem. Stability tests by NCAR-HCMTS confirmed this assumption using both standards and whole air samples, provided that the pressure within the canister was always maintained above 760 torr. To help ensure that the canister cleaning manifold was functioning effectively, one canister from each cycle (20 canisters were cleaned during each cycle) was checked for cleanliness.

## ATLANTA INTENSIVE

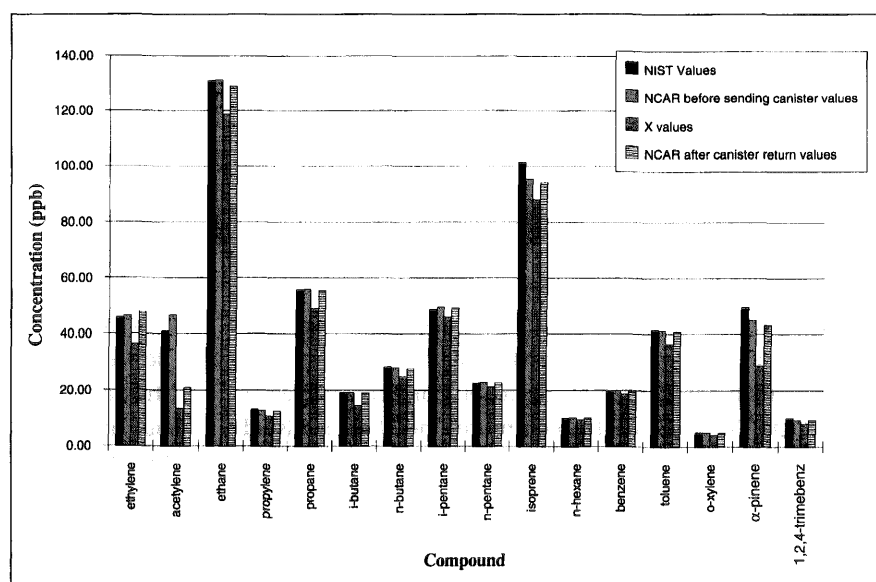
### Standards Provided for the Intensive

The protocol developed by the participating research groups called for three standard mixtures to be deployed by each group at each site: gravimetric calibration standard, retention index standard, and internal standard. The gravimetric calibration standard was purchased from NIST; it contained n-butane and benzene at approximately 10 ppbv each in high-purity N<sub>2</sub> balance gas. The stated accuracy was approximately  $\pm 2\%$  for each compound. The retention index standard was made by Scott Specialty Gases, and it contained all 56 targeted priority hydrocarbons and halocarbons listed in Table 1. The balance gas was high-purity N<sub>2</sub>. The concentration for each hydrocarbon was approximately 30 ppbv except for the n-alkanes, which had a concentration of approximately 60 ppbv. The internal standard was also made by Scott Specialty Gases and contained the four compounds (in N<sub>2</sub> balance gas) mentioned previously: 1,1-difluoroethylene (50 ppbv), 2,2-dimethyl butane (15 ppbv), 3-fluorotoluene (15 ppbv), and n-decane (10 ppbv). All standards were provided in Scott CL Series Aculife-treated cylinders at approximately 2000 psi.

The standard operating procedure used by all participants for each sampling day included the following activities. At the beginning of the day, a zero blank was analyzed, followed by the 56-component retention index mixture and the NIST gravimetric standard. This enabled each participant laboratory to (1) ensure that its system was operating cleanly, (2) track the identification efficiency of the instrument and ensure that all 56 compounds were falling within the specified windows, and (3) track the changes in calibration throughout the Intensive and ensure that the calibration was correct during every day of the Intensive. This analysis procedure was modified slightly during the Intensive. The retention index mixture was run at the end of the day rather than at the beginning because of observed carryover problems resulting from the high concentrations of some compounds in the mixture, into the first ambient run of the day. The four-component internal standard mixture was injected with every GC sample.

### Challenge Mixtures Distributed During the Intensive

During the Intensive, the NCAR-HCMTS group provided challenge mixtures to participants to help determine if the various deployed instruments were operating satisfactorily. Two challenge mixtures were available: a NIST 16-component gravimetric standard, and an analyzed whole air sample provided by AREAL/EPA. These mixtures were run periodically during the intensive in exactly the same way as a collected ambient sample. Before and after distribution to participants, the samples were analyzed by NCAR-HCMTS and AREAL/EPA. This was done to track potential changes in the concentration over time.



**Figure 2.** Example of the report information supplied to a participant X for the 16-component gravimetric challenge sample. The X values can be compared to NIST values, as well as to NCAR-HCMTS values obtained before sending out canister and after canister return.

**Table 2.** International hydrocarbon intercomparison planning committee.

Scientist	Organization
Jack G. Calvert	Committee chairman, IGAC coconvenor of the International Nonmethane Hydrocarbon Intercomparison Experiment, Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO
Fred Fehsenfeld	Committee cochairman, IGAC coconvenor of the International Nonmethane Hydrocarbon Intercomparison Experiment, NOAA, Aeronomy Laboratory, Boulder, CO
Bernard Bongsang	Centre des Faibles Radioactivités, Dodmaine du CNRS, Gif-sur-Yvette, France
William Dorko/Gerry Rhoderick	National Institute for Standards and Technology, Gaithersburg, MD
Paul Goldan	NOAA, Aeronomy Laboratory, Boulder, CO
James Greenberg	Atmospheric Chemistry Division, NCAR, Boulder, CO
Gerald L. Gregory	NASA, Langley Research Center, Hampton, VA
William Lonneman	Environmental Protection Agency Technical Center, Research Triangle Park, NC
Jarvis Moyers	National Science Foundation, Washington, DC
Hiromi Niki	Center for Research Atmospheric Chemistry, York University, North York, ON, Canada
David D. Parrish	NOAA, Aeronomy Laboratory, Boulder, CO
Stuart A. Penkett	School of Environmental Sciences, University of East Anglia, Norwich, England
Rei Rasmussen	Oregon Graduate Institute, Beaverton, OR
James Roberts	NOAA, Aeronomy Laboratory, Boulder, CO
Jochum Rudolph	Institut für Chemie 3, Atmosphärische Chemie der Kernforschungsanlage, Jülich, Germany
Wolfgang Seiler/Jürgen Hahn	Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen, Germany
Hanwant B. Singh	NASA Ames Research Center, Moffett Field, CA
Hal Westberg	Air Pollution Research Laboratory for Atmospheric Research, Washington State University, Pullman, WA
Peter T. Woods/Roger Partridge	National Physical Laboratory, Middlesex, England
Patrick Zimmerman	Atmospheric Chemistry Division, NCAR, Boulder, CO

IGAC - International Global Atmospheric Chemistry

NCAR - National Center for Atmospheric Research

CNRS - Centre National de la Recherche Scientifique

NOAA - National Oceanic and Atmospheric Administration

**16-Component Standard.** The NIST standard contained 16 components shown on the x-axis of Figure 2. The components of the mixture were selected through discussions and planning by the IHIC Committee (overseeing committee of the NOMHICE program). The committee members are listed in Table 2. These mixtures were received from NIST in five separate high-pressure aluminum (Acuflex-treated) cylinders, each with a somewhat different concentration. Participating laboratories were asked to identify and quantify the 16 hydrocarbon compounds present in the mixture.

Figure 2 illustrates how typical results are presented for each of the participant laboratories. NIST gravimetric

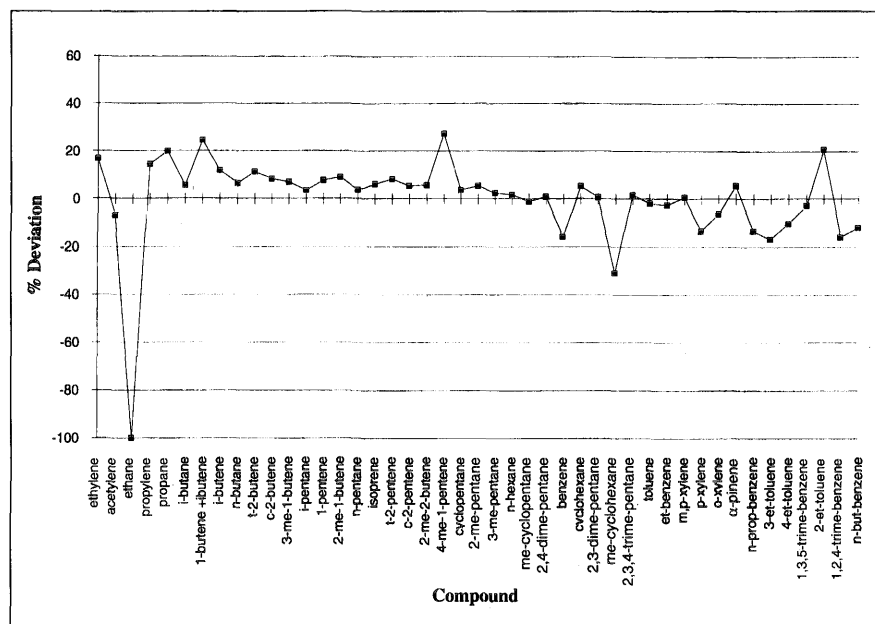
values are given in the first bar for each compound. The second bar gives values obtained by NCAR-HCMTS before delivering the canister to laboratory X. The third bar gives the values obtained for this particular canister by the participating laboratory. The fourth bar gives values obtained by NCAR-HCMTS after the canister was returned to NCAR for reanalysis. Acetylene decreases with time in some of the canisters, and  $\alpha$ -pinene decreases with time in all of the canisters. The agreement between NIST and NCAR-NOMHICE initially is quite good for all of the compounds. Analysis of this standard provided a means to check on the scientists' ability to identify and quantify compounds that span the

entire required range of measurement. Analyses from all participant sites showed that the analytical systems employed could easily identify, in an automated fashion, all compounds present in the mixture.

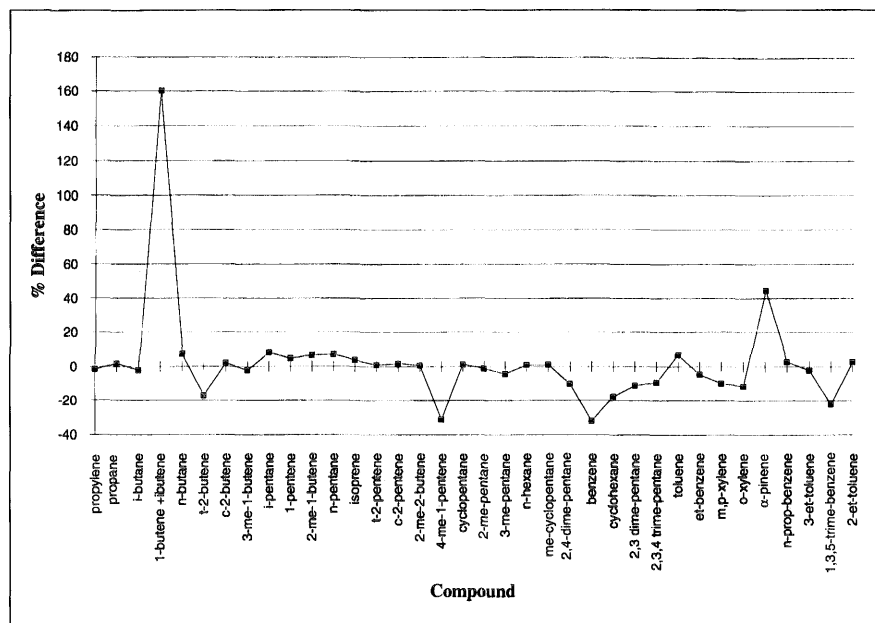
**Whole Air Sample.** The ability of participating laboratories to identify and quantify the 56 target compounds in ambient air was determined by analysis of the whole air sample. Figure 3 shows the utility of this procedure. This figure represents the comparison between one participant (Site 2) with

NCAR-HCMTS for selected target compounds. Not all 56 target compounds were found in the ambient air sample. NCAR-HCMTS observed 52 target "peaks," whereas the participant laboratory observed 46 target compounds. Some of the target compounds were at or near the detection limit of the participant's instrument. The compound is plotted against the percentage deviation observed by the site from NCAR-HCMTS values. For most compounds, the agreement is satisfactory. However, for ethane, the agreement is extremely poor. The reason for this discrepancy was that the

Entech instrument was not efficiently trapping ethane. Experiments on an identical instrument had shown that setting the trap temperature to  $-165^{\circ}\text{C}$  was sufficient to trap all of the  $\text{C}_2$  compounds (including ethane, the most difficult of the  $\text{C}_2$  compounds to trap). However, there were slight differences from instrument to instrument in the trap temperature setting of the instrument and the true temperature of the trap. When the trapping temperature was set to  $-180^{\circ}\text{C}$  the problem disappeared. Figure 4 shows another example of the utility of this methodology. As in Figure 3, this plot represents the comparison between a participant (Site 3 in this case) with NCAR-HCMTS. In this case, a large discrepancy for 1-butene indicates contamination from some source. The cause of this contamination is uncertain at this time.



**Figure 3.** Percentage deviation vs. NCAR-NOMHICE for a whole air sample challenge mixture circulated to site scientists and analyzed during the intensive. This data represents results from one of the sites on Aug. 12, 1992.



**Figure 4.** Percentage deviation vs. NCAR-NOMHICE for a whole air sample challenge mixture circulated to site scientists and analyzed during the intensive. This data represents results from one of the sites on Aug. 14, 1992.

## CONCLUSIONS

A major component of the Southern Oxidants Study 1992 Atlanta Intensive was the measurement of atmospheric NMHC compounds. The SOS science team targeted for quantitative analysis 56 compounds, many of which may be substantial contributors to ozone formation. Automated gas chromatographic systems were chosen to make the measurements. A quality assurance program was instituted to help ensure that accurate and precise measurements were made for each target compound throughout the network. This program involved deployment of a series of standards that were analyzed by all participants each sampling day to ensure the correct calibration of the instrument and



correct retention time windows for identification of the target compounds. The performance of the instruments was further evaluated through the periodic analysis of challenge mixtures. One challenge mixture was an NIST gravimetric standard; the other was a whole air sample. Challenge mixtures such as these are invaluable for assessing overall data integrity and should be an integral part of any large-scale field measurement program. The strategy employed appears to have helped considerably in ensuring quality measurements. Canister samples analyzed by the reference laboratory prior to and after analysis by the participant laboratories were particularly useful to compare analysis systems and to evaluate the storage of air samples in canisters.

## ACKNOWLEDGMENTS

Support for this research was provided by the Southern Oxidants Study through the Atmospheric Research and Exposure Assessment Laboratory of the U.S. Environmental Protection Agency and in part by the Atmospheric Chemistry Project of the National Oceanic and Atmospheric Administration Climate and Global Change Program. We gratefully acknowledge the help of the following scientists, without whom this work could not have been completed: Z. Li, M. Das, and B. Hartsell of NCSU; C. Farmer, D. Riemer, and P. Milne of UM RSMAS; C. Stoneking, L. Garland, R. Strekowski, and D. Gatti of GIT; Bob Imhoff of TVA; and J. Martinez of TVA and GIT.

## REFERENCES

- Chameides, W.L.; Fehsenfeld, F.; Rodgers, M.O.; Cardelino, C.; Martinez, J.; Parrish, D.; Lonneman, W.; Lawson, D.R.; Rasmussen, R.A.; Zimmerman, P.; Greenberg, J.; Middleton, P.; Wang, T. "Ozone precursor relationships in the ambient atmosphere," *J. Geophys. Res.* **1992**, *97*, 6037.
- Carter, W.P.L. "A detailed mechanism for the gas-phase atmospheric reactions of organic compounds," *Atmos. Environ.* **1990**, *24A*, 481.
- Carter, W.P.L. "Development of ozone reactivity scales for volatile organic compounds," U. S. Environmental Protection Agency, 1991; EPA 600/3-91-050.
- Jensen, T.E.; Siegl, W.O.; Richert, J.F.O.; Lipari, F.; Loo, J.F.; Probst, A.; Sigsby, J. "Advanced Emission Speciation Methodologies for the Auto/Oil Air Quality Improvement Research Program - I. Hydrocarbons and Ethers"; Society of Automotive Engineers; SAE Technical Paper No. 920320, Detroit, MI, 1992.
- Holdren, M.W.; Smith, D.L. "Performance of Automated Gas Chromatographs Used in the 1990 Atlanta Ozone Study"; in Proceedings of the 1991 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants; Air & Waste Management Association, Pittsburgh, 1991.
- Lonneman, W.A.; Seila, R.L.; Daughtridge, J.V.; Richter, H.G. "Results from the Canister Sampling Program Conducted During the 1990 Atlanta Precursor Study"; in Proceedings of the 84th Air & Waste Management Association Annual Meeting, Vancouver, BC, Canada, 1991; Paper No. 91-68.2.
- Shreffler, J.H. "Comparison of Non-Methane Organic Compound Concentration Data Collected by Two Methods in Atlanta," *J. Air & Waste Manage. Assoc.* **1993**, *43*, 1576.
- Goldan, P.D.; Kuster, W.C.; Montzka, S.A.; Fehsenfeld, F.W. "Atmospheric hydrocarbons in a rural Alabama pine forest," *EOS Trans. AGU* **1990**, *71*, 1228.
- Bernardo-Bricker, A.; Farmer, C.T.; Milne, P.J.; Reiner, D.D.; Zika, R. "Validation of speciated nonmethane hydrocarbon compounds collected during the Atlanta Intensive 1992 as part of the Southern Oxidants Study (SOS)," submitted for publication in *J. Air & Waste Manage. Assoc.*
- Greenberg, J.P.; Zimmerman, P.R. "Nonmethane hydrocarbons in remote troposphere," *J. Geophys. Res.* **1984**, *89*, 4767.
- Apel, E.C.; Calvert, J.G.; Fehsenfeld, F.W. "The non-methane hydrocarbon intercomparison experiment (NOMHICE): Tasks 1 and 2," accepted for publication in *J. Geophys. Res.*, 1994.
- Rhoderick, G., private communication, 1993.
- Martinez, J.E. "Impact of natural and anthropogenic hydrocarbons on tropospheric ozone production: Results from automated gas chromatography"; Ph.D. dissertation, Georgia Institute of Technology, 1992.
- Farmer, C.T.; Milne, P.J.; Riemer, D.D.; Zika, R.G. "Continuous hourly analysis of C2-C10 non-methane hydrocarbons compounds in urban air by GC-FID," *Environ. Sci. Technol.* **1994**, *28*, 2:238.
- Leveque, R.E. "Determination of C<sub>3</sub>-C<sub>8</sub> hydrocarbons in naphtha and reformates utilizing capillary column gas chromatography," *Anal. Chem.* **1967**, *39*, 1811.
- Ackman, R.J. "The flame ionization detector: Further comments on molecular breakdown and fundamental group response," *J. Gas Chromatogr.* **1968**, *6*, 497.
- Blades, A.T. "Ion formation in hydrocarbon flames," *Can. J. Chem.* **1976**, *54*, 2919.

## About the Authors

E.C. Apel, Ph.D., and J.G. Calvert, Ph.D., are scientists in the Atmospheric Chemistry Division, National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80303.

R. Zika, Ph.D., is a Professor in the Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, FL.

M. Rodgers, Ph.D., is an associate professor and director of Air Quality Laboratory in the School of Earth and Atmospheric Sciences at the Georgia Institute of Technology, Atlanta, GA.

V. Aneja, Ph.D., is a research associate professor in the Department of Marine, Earth, and Atmospheric Sciences at the North Carolina State University, Raleigh, NC.

J. Meagher, Ph.D., is manager of the Atmospheric Science Department at the Tennessee Valley Authority, Muscle Shoals, AL.

W. Lonneman, Ph.D., is a scientist at the Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC.