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Lawrence Berkeley Laboratory
Applied Science Division

NEWSLETTER

JANUARY/FEBRUARY 1985

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FEATURED PUBLICATION

The Science of the Total Environment, 36: 271-276 (1984)

DETERMINATION OF ORGANIC OXYGEN IN AMBIENT PARTICULATE MATTER

W.H. Benner, A.D.A. Hansen, L.A. Gundel, and T. Novakov

ABSTRACT: A sample of ambient particulate matter is pyrolyzed in N_2 at 1135°C, and the evolved oxygen is detected by nondispersive infrared spectrometry after conversion to CO. Oxygen in organic compounds, carbonates, silicates, sulfates, nitrates, water, and adsorbed oxygen-containing gases is quantitated; but silica and alumina are not detected. Organic oxygen is determined by analyzing an evaporated extract of the sample. A procedure is also presented for determining oxygen thermograms. The organic fraction of ambient particulate matter is highly oxygenated (C/O 2).

The following is from a discussion with Henry Benner:

ASD: Why are you interested in organic oxygen?

Henry: Our main concern is particulate matter in the atmosphere. We are attempting to find out why haze is formed. Haze is due to light scattered from particles, and that means that if we want to understand haze we need to understand something about the particles. We would like to know the origin and pertinent physical properties of the particles -- their size distributions, how much light they scatter or absorb, and their composition. Some of the particles that scatter light are created by atmospheric chemical reactions; other particles are produced simply by combustion. For example, soot particles are spewed out by cars or smokestacks. Chemical reactions in the atmosphere that lead to the formation of particles are referred to as "smog-type" chemical reactions. Reactants in smog-type reactions include gaseous hydrocarbons, nitrogen

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oxides, sulfur dioxide, ozone, and some other trace gases in the atmosphere.

Some of the smog-type reactions are photochemical, that is, they are initiated by sunlight. Ozone in the urban atmosphere, for example, is the result of photochemical reactions. Other photochemically initiated reactions may lead to a partial oxidation of gaseous hydrocarbons, which then condense out of the atmosphere onto already existing particles or to nucleate new particles.

We are interested in organic oxygen in the particles because we would like to know if oxidized organic materials formed in the atmosphere condense onto existing particles or nucleate to form new particles. We are trying to understand the reaction mechanisms that convert gaseous hydrocarbons into particulate matter that scatters light. Scientists who have been studying air pollution pretty much know what the reactants are. They know the hydrocarbons are present and they know that certain oxidizing mechanisms probably exist, but the actual conversion of hydrocarbon gases into particulate matter has been more of a theory. Some smog chamber studies have tried to test such a theory, but the documentation of such mechanisms in the atmosphere has never been adequately done.

ASD: To measure the content of organic oxygen in particulate matter you collect the particles in filters and you pyrolize the samples. Can you be absolutely certain that by pyrolizing samples you will measure all of the organic oxygen present in these samples?

Henry: We have analyzed a whole series of oxygen-containing compounds that have been identified in particulate matter, and we have found that the recovery is pretty close to 100% for all of them. So we know that we can measure all organic oxygen contained in molecules typically found in ambient particulate matter.

ASD: In your paper you discuss procedures for determining oxygen thermograms. What is a thermogram, and what information can be obtained from a thermogram?

Henry: There are various thermal methods used in chemical analysis. In the technique that we have developed, we measure the amount of oxygen that evolves from the sample as it is heated from room temperature up to about 1000° C. We developed the thermal analysis technique so that we could make some broad classifications of oxygenated organic materials. In terms of the smog reactions that I described earlier, the hypothesis is that oxygenated materials which condense out of the gas phase have a fairly low molecular weight and a fairly high vapor pressure--somewhat volatile but not as volatile as the original gaseous hydrocarbon. We can determine how volatile these compounds are by determining the temperature at which they are

released from the filter sample. The material that is floating around in the air contains a whole variety of oxygenated compounds, and to identify each one of them would be a rather complicated task. We are trying to eliminate the need to speciate each oxygenated compound and instead get a general idea of the classification of oxygenated material: whether the compounds have a low, medium or high vapor pressure.

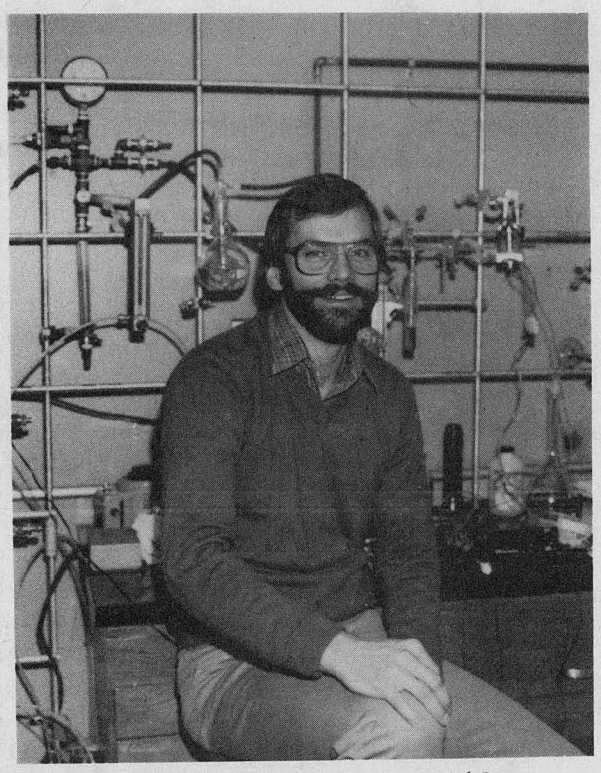
ASD: Could you give us examples of such compounds?

Henry: Scientists who have collected particles from so-called "smog-chamber" experiments have identified oxygenated-organic compounds of fairly low molecular weight; some could be C_4 or C_5 hydrocarbons with one or two carboxylic acid groups on them. These types of compounds can be solids or liquids at room temperature, and when analyzed by the thermal analysis method, should be released in the range of 50° to $250^{\circ}C$. When you consider the reactions that proceed in the atmosphere, you can identify products that would condense out at ambient temperatures because of their vapor pressures. If that were the case, then they would perhaps be desorbed from the sample at $50^{\circ}C$ rather than $200^{\circ}C$. Interestingly enough, as we analyze samples of ambient particulate matter, we see that there is very little oxygen that comes off of the sample below $200^{\circ}C$. Most of it comes off the sample between $200^{\circ}C$ and $800^{\circ}C$, indicating that much of the oxygen is contained in compounds of low volatility.

ASD: How do you intend to pursue these studies?

Henry: We have far from clarified the questions that were asked initially. Basically, this paper describes two techniques for measuring organic oxygen in ambient particulate matter. This type of analysis could not be done earlier because previous methods required milligrams to grams of samples, while our methods permit us to analyze micrograms of material. This is critical since it is difficult to collect large quantities of ambient particulate matter. In this paper, only a few analyses of ambient particulate matter were reported. Many more need to be analyzed. In addition, we have also analyzed solvent extracts of ambient particulate matter and want to do more analysis of extracts. We plan to proceed in two directions. In the first, we want to study particles collected from different areas; that means we might collect samples in the Caldecott Tunnel and compare them with samples collected on a smoggy day in Los Angeles. We will analyze these samples to look at oxygen-to-carbon ratios. If indeed smog-type reactions occur which oxidize gaseous hydrocarbons to produce oxygenated organic matter, then we should see an increase in the oxygen-carbon ratio proportional to the amount of time the particles reside in an oxidizing atmosphere. We would expect a fairly low oxygen-to-carbon ratio in samples from the Caldecott Tunnel and that this ratio would increase as particles pick up more oxygenated material in the atmosphere. In the

second direction we will study combustion-generated soot particles. These are expected to have a fairly low oxygen-to-carbon ratio. Although soot is formed because of incomplete combustion, these particles generally do not have very much oxygen associated with them (preliminary evidence from a few samples that we have analyzed indicates this). We don't know what factors influence the oxygen-carbon ratio in soot particles. We would also like to see how flame conditions influence this ratio.



HENRY BENNER IN HIS LAB

THIRD FLOOR CONFERENCE ROOM

The reservation system for the 3rd floor conference room (Bldg. 90-3148) is now being handled by the Applied Science Division receptionist, Angela Smothers (x5001). The key and signout book for the projection room are also being kept by Angela. This new arrangement is for convenience; the room remains a Lab-wide facility and all groups within the Laboratory have equal access.

DAYLIGHT SIMULATION FACILITY RECEIVES PROGRESSIVE ARCHITECTURE AWARD

The Windows and Daylighting Group, headed by Steve Selkowitz, received a citation from Progressive Architecture for their Daylight Simulation Facility which is located at the College of Environmental Design on the U.C. Berkeley campus. The 32nd annual P/A Awards presentation was held on Jauary 25, 1985 in the Grand Ballroom of the Plaza Hotel in New York City. There were 31 winners out of a total of 933 submissions.

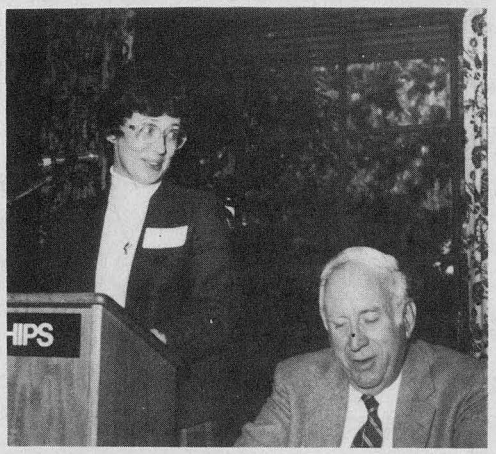
Daylighting, especially for commercial buildings, offers one of the most effective ways of reducing energy consumption. The development of the daylight simulator allows the study of more complex buildings, the testing of both thermal and luminance daylighting effects, and the development of new design tools. The simulator's primary use is for DOE research, but it is also available to architecture firms on a limited basis. A summary report on the Daylight Simulation Facility can be obtained from Michael Wilde (x6847).

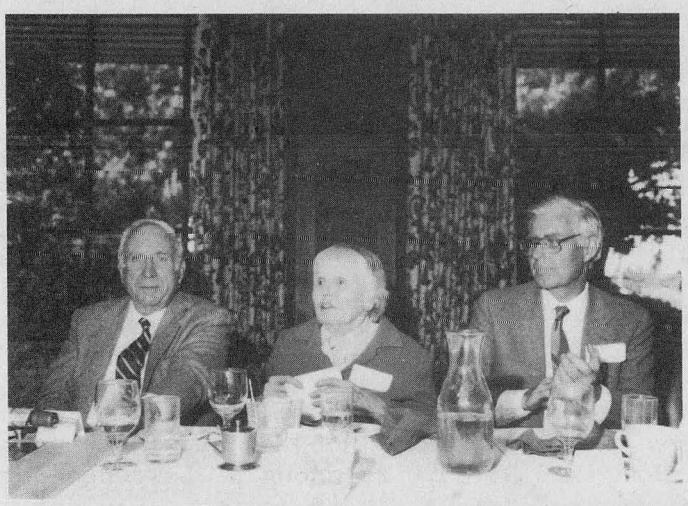
HONORS

One of the papers presented by Shih-Ger Chang and David Littlejohn at the PAC CHEM meeting in Honolulu in December 1984 has been selected to appear in the newsbrief section of the January 7, 1985 issue of Chemical & Engineering News. The following is an excerpt from that newsbrief section:

> Flue Gas Scrubbing Liquors May Contain Poisons
>
> "The scrubbing liquors accumulated in the operation of wet flue gas desulfurization systems are likely to contain toxic compounds, according to Shih-Ger Chang and David Littlejohn of Lawrence Berkeley Laboratory. Of particular concern are the nitrogen-sulfur compounds formed by reactions among nitrogen oxides, sulfur dioxide, water, and other components of the scrubbing liquor. Chang and Littlejohn have been using a number of techniques, including laser Raman spectrometry, differential pulse polarography, and ion chromatography to check for several compounds, such as hydroxylamine, sulfamic acid, hydroxylamine mono- and disulfonates, and amine di- and trisulfonates. They have found one or more of the compounds in most of the scrubbing liquor samples they have tested. Hydroxylamine and sulfamic acid are known to be toxic, they note. Although toxicities of the other compounds are unknown, it is known that these compounds will hydrolyze to hydroxylamine or sulfamic acid under acidic conditions. Thus, the Lawrence Berkeley scientists conclude, spent scrubbing liquors should be disposed of with due care."

SCENES FROM AMOS NEWTON'S RETIREMENT PARTY





CONGRATULATIONS!

- To Jan Smith and Bruce Barrows on the birth of their son, Drew Virgil, on January 19, 1985. (Bruce claims that the date of birth was auspicious for the 49'ers in Superbowl 19 -- but then, why didn't they name their child Joe, Dwight or Wendell?)

- To Peter and Peggy Cleary on the birth of their first child, a nine pound, 14 ounce daughter. Her name is Alison Clare, and she was born at Kaiser Hospital in San Francisco on January 10, 1985.

TECHNOLOGY TRANSFER

Michael Wilde was invited to participate in an ASHRAE/DOE Roundtable on Technology Transfer on December 12-14 in Washington, D.C. Sponsored by the Building Systems Division of DOE, this three-day roundtable brought together 45 building industry representatives involved in shaping research utilization policy to identify constraints and make recommendations for improving dissemination of a broad base of information.

The group divided into three subpanels arranged by user groups; design professionals, product manufacturers and trade associations, and building users and code officials. The subpanels identified potential actions to upgrade and refine both the public and private sector implementation of technology transfer. Special attention was given to a more efficient penetration of the user market, as well as the technical information flow process. A final report will be published by ASHRAE/DOE in February 1985.

AIR INFILTRATION CENTRE CONFERENCE

Harrah's Hotel in Reno, Nevada provided a colorful setting for the Air Infiltration Centre's 5th Annual Conference held on October 1-4, 1984. Carol Stoker, from the Energy Performance of Buildings (EPB) research group, was responsible for the conference organization. The theme of the conference was air infiltration standards, and over 70 attendees from 12 countries attended the meeting, including invited speakers from Japan and Germany.

The keynote address was presented by John Millhone, Director of the Office of Building Energy Research and Development at the U.S. Department of Energy in Washington, D.C. The focus of the address was on the role of air infiltration in energy conservation. Millhone highlighted the significance of this topic by pointing out that a 1% reduction in infiltration and ventilation rates would reduce annual U.S. energy costs by approximately $300 million. He also stated that the thrust of American infiltration and ventilation research is intertwined with many energy conservation research activities, the most current of which is commercial building systems integration. Other important areas include retrofit of existing buildings, indoor air quality studies and residential building systems.

Max Sherman, EPB researcher, and Jorn Brunsell, visiting researcher at LBL from the Norwegian Building Research Institute, gave presentations addressing the question of airtightness standards and the consequences of such standards.

INVITED TALKS AND FOREIGN TRAVEL

December

- Nabil Amer traveled to Southern California twice this month: first, to present a USC Physics Department colloquium on "Recent Advances on Photothermal Spectroscopy and its Applications"; and second, to deliver a talk on "Photothermal Imaging of Thin Films and Optical Coatings" at a Defense Advanced Research Project Agency (DARPA) program review at the Naval Weapons Center in China Lake.

- Elton Cairns delivered an invited lecture at Texas A&M University. His presentation was entitled "Electrochemical Energy Conversion and Storage."

- Elizabeth Griffiths and David Littlejohn traveled to Hawaii to present papers at the 1984 International Chemical Congress of Pacific Basin Societies, sponsored by the American Chemical Society. Griffiths spoke on "Quantum Yield Determination of the Photoreduction of Ferric Chelates by Means of Brown Ring Formation Technique," and Littlejohn spoke on "Determination of Products and Mechanism of the Reaction of Ferrous Nitrosyl Chelates with Sulfite Ion."

- Steve Selkowitz was invited to address the National Research Council in Ottawa, Canada. The subject of his talk was the ASD Windows and Daylighting research program.

- Rudy Verderber addressed the Sub-Committee on Electromagnetic Radiation of the National Electrical Manufacturers Association (NEMA) convention in Washington, D.C. The title of his talk was "Electromagnetic Interference from Fluorescent Lighting Operating with Solid State Ballasts in Various Sites."

- Michael Wilde was invited to participate in a Southern California Daylighting Council meeting in Los Angeles. The Council, which is currently formalizing its relationship with a national network of other such groups, was particularly interested in Wilde's experience with technology transfer.

January

- Mark Modera attended the ASHRAE Winter Meeting in Chicago where he presented a paper entitled "Technical Description: the Envelope Thermal Test Unit."

- Andrea Ketoff traveled to Mexico City to gather information on energy demand in the country and to meet with representatives of PEMEX, the Mexican national oil company, and SEMIP, the Secretary of Energy and Mines, concerning interaction between LBL, DOE, and the Mexican government. For similar purposes, Lee Schipper met with officials of the Venezuelan Ministry of Energy in Caracas.

RECENT REFEREED JOURNAL ARTICLES

R.H. Fish, J.L. Tan, and A.D. Thormodsen, "Homogenous Catalytic Hydrogenation. 2. Selective Reduction of Polynuclear Heteroaromatic Compounds Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)," J. Org. Chem., 49, 4500-4505 (1984).

Fish, Richard H., John J. Komlenic, and Brian K. Wines, "Characterization and Comparison of Vanadyl and Nickel Compounds in Heavy Crude Petroleums and Asphaltenes by Reverse-Phase and Size-Exclusion Liquid Chromatography/Graphite Furnace Atomic Absorption Spectrometry," Analytical Chemistry, 56, 2452-2460 (1984).

Benner, W.H. and A.D.A. Hansen, "Temperature-Programmed Evolved Gas Analysis for Determining Pyrolyzable Oxygen," Analytical Chemistry, 56, 2876-2879 (1984).

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Lampert, Carl M., "Electrochromic Materials and Devices for Energy Efficient Windows," Solar Energy Materials 11, 1-27 (1984).

Xu, X.B. and S.G. Chang, "Study of the Disproportionation of Sodium Thiosulfate by X-Ray Photoelectron Spectroscopy," High Temperature Science, 17, 165-170 (1984).

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Gerlach, Robert, Dianyuan Wei, and Nabil M. Amer, "Coupling Efficiency of Waveguide Laser Resonators Formed by Flat Mirrors: Analysis and Experiment," IEEE Jour. of Quantum Electronics, Vol. QE-20, No. 8, 948-963 (August 1984).

Navvab, M., M. Karayel, E. Ne´eman, and S. Selkowitz, "Daylight Availability Data for San Francisco," Energy and Buildings, 6, 273-281 (1984).

Johnson, R., R. Sullivan, S. Selkowitz, S. Nozaki, C. Conner, and D. Arasteh, "Glazing Energy Performance and Design Optimization with Daylighting," Energy and Buildings, 6, 305-317 (1984).

Ne´eman, E., "A Comprehensive Approach to the Integration of Daylight and Electric Light in Buildings," Energy and Buildings, 6, 109-118 (1984).

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