NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
TECHNOLOGY APPLICATION TEAM PROGRAM

CASE FILE COPY

SUMMARY FOR MONTH ENDING 30 NOVEMBER 1972

RTI TATeam

Environmental Technology
SUMMARY FOR MONTH ENDING 30 NOVEMBER 1972

This summary is for the timely communication of contacts between the RTI TATeam and the National Aeronautics and Space Administration (NASA), the Environmental Protection Agency (EPA), and other governmental, educational, and industrial organizations participating in NASA's Technology Utilization Program.

This summary is submitted for the use of NASA's Technology Utilization Division, Technology Utilization Officers located at NASA Field Centers, and other individuals participating in or interested in the Technology Utilization Program. If you have any suggestions or questions related to the activities reported here, please call or write any RTI TATeam member at the above address.
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ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems

A. RTI/AP-10/26, Development of Advanced Pollutant Sensor for Methane and Total Hydrocarbons

Date: 11/1/72  
Type of Contact: Correspondence  
Person Contacted: R. P. Donovan  
By: MSFC  
A & PS-MS-D  
Huntsville, Alabama 35812

Summary of Contact: Received (1) "Report of Functional Testing on GE Tungsten Oxide Hydrogen Detectors", 54TR2-50M17522, 12/14/71, and (2) "Gaseous Hydrogen Detectors, Tungsten Oxide, Test Procedure For", 54TR2-02-50M17522, 11/23/71. These documents are related to the thin film hydrocarbon detectors also built by GE (but of indium sesquioxide) and now ready for test by Hafner and co-workers at MSFC.

B. RTI/AP-27, Development of Advanced Pollutant Sensor for Carbon Monoxide

Date: 11/7/72  
Type of Contact: Correspondence  
Person Contacted: R. P. Donovan  
By: Don Willet  
Director of Marketing  
ANDROS Inc.  
2332 Fourth Street  
Berkeley, California 94710

Summary of Contact: Received product information and glossy prints of the ANDROS 7000 CO Analyzer. Also included were a list of advertisements including the number of inquiries generated, a reprint from Science and a preprint of an article to appear in the Nov. R/D magazine. This information will be forwarded to Todd Anuskiewicz. (See Appendix A).

Date: 11/7/72  
Type of Contact: Correspondence  
Person Contacted: Todd Anuskiewicz  
By: R.P. Donovan

Summary of Contact: Forwarded the ANDROS information and pictures to Todd in response to his request of last month. (Appendix A)
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (cont'd)

Date: 11/7/72
Type of Contact: Correspondence
Person Contacted: Charles Eastwood
NASA Headquarters
By: R. P. Donovan

Summary of Contact: Carbon copy of letter and enclosures (no Pictures) (Appendix A) received from Don Willet, Andros, sent to Charlie.

Date: 11/9/72
Type of Contact: Telephone
Person Contacted: ANDROS Inc.
By: R.P. Donovan

Summary of Contact: Left message for Don Willett to the effect that I would call next week to learn: (1) Patents covering the ANDROS 7000 and (2) The NASA/EPA contribution to the instrument development.

Date: 11/9/72
Type of Contact: Telephone
Person Contacted: Todd Anuskiewicz
By: R. P. Donovan

Summary of Contact: Todd inquired as to the patent status of the ANDROS 7000. I replied that the patents belonged to Arkon but that NASA had paid for the transition from patentable concepts to flight hardware. I promised to confirm this statement with Don Willet of ANDROS and to obtain the numbers of any issued patents related to the ANDROS CO monitor. In addition, I agreed to once again go over the history of the instrument development with Don Willet in an effort to clearly define the roles played by EPA, NASA, and Arkon.

Date: 11/14/72
Type of Contact: Telephone
Person Contacted: R. P. Donovan
By: Don Willet, ANDROS

Summary of Contact: Don called in response to my questions of last Friday regarding the patent background and history of the development of the CO monitor. No patent has yet been issued but one is expected in about 3 or 4 months. It was filed on Sept. 19, 1969 serial number 859326 under the title "A Fluorescent Source Nondispersive Infrared Gas Analyzer". The patent is in the name of Bill Link, is assigned to Arkon Scientific Laboratory, and contains 27 claims, chiefly on the use of isotopes of CO, CO in combinations with other gases, and isotopes of other gases as fluorescing sources in NDIR methods of pollution detection.
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (Cont'd)

Don had a list of contracts under which the CO monitor was developed. He plans to forward this list to me to aid in any evaluation of who did what, when and who paid for it. The list contains a host of NASA contracts but does include two NAPCA contracts, one of which was for fluorescent source CO development.

Hartlege and Tom Pardue in the Surveillance Division of EPA, RTP are expected to order a CO monitor shortly. The EPA people in Ann Arbor already have one. The Langley unit should be shipped this Friday (11/17/72). This unit will end up in Bob Stevens' hands eventually.

TU paid for the sub-contract that Arkon had to provide Perkin-Elmer with two CO units as part of a cabin atmosphere monitor system bought by the Navy. This Perkin-Elmer system included a mass spectrometer that also was supported by TU. The Navy experience on submarines has been so good that the Navy is planning to order 38 more around the first of the year. This number could increase to 200 or so eventually.

The Navy is also interested in an early warning fire detection system. They envisalize a CO monitor much like the ANDROS unit which will detect higher levels of CO (on the order of 100 ppm) but which will cost substantially less ($1,000 to $4,000). ANDROS feels confident they can build this but acknowledge that some re-engineering development would have to be done. Don inquired as to whether NASA TU would be a source of funds for this development, claiming that the impact of having such NASA developed units on every sub would be considerable.

I promised to follow up with TU Headquarters on his inquiry but warned that cost sharing with the Navy or other Defense Department agencies seemed more removed from the TU mission of transferring space technology into the public domain than usual. Don immediately responded with the fact that the Bureau of Mines outside of Pittsburgh (Bruceton) also has an interest in early warning fire detection systems utilizing this system and that if this group would be more palatable to TU that too would be fine with ANDROS.

I told Don of the Abt Assoc. problem in early warning fire detection systems and their approach via the MIT proposal. The big difference of course is that the MIT group envisions a detector costing less than $50 eventually while the ANDROS instrument seems destined to be at least an order of magnitude more expensive.

Date: 11/17/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Don Willett
ANDROS Inc.
2332 Fourth St.
Berkeley, Cal. 94710
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (Cont'd)

Summary of Contact: Received (1) A contract history of Gas Analysis at ANDROS and (2) A reprint for the Nov. 72 R/D magazine, "Improved Fluorescence Analysis", F.W. Karosek, p. 36 - 37.

Date: 11/17/72
Type of Contact: Telephone
Person Contacted: Charlie Eastwood
By: R. P. Donovan

Summary of Contact: Advised Charlie of ANDROS' interest in re-engineering a CO monitor as an early warning fire detector system. The Navy is interested in having a less sensitive but much cheaper unit than the ANDROS 7000. Such an instrument, if successful, could have large public sector impact. Charlie encouraged a proposal.

Told Charlie that Jim Brown had determined that the ERC partial detector, as reported in an IITRI report, was obsolete and no solution to FCP-3.

Requested another copy of the LeRC memo along with the authors FTC numbers (for Dick Thompson at EPA).

Date: 11/17/72
Type of Contact: Telephone
Person Contacted: Don Willett
By: R. P. Donovan

Summary of Contact: Thanked Don for sending me the contract history on the ANDROS 7000. Told Don of Charlie's encouragement to submit a proposal for an early warning fire detector system to NASA TU. Don said he could hand carry such a proposal the week of December 4th. I agreed to tip Charlie off in advance so that he is prepared.

Date: 11/20/72
Type of Contact: Telephone
Person Contacted: Charlie Eastwood
By: R. P. Donovan

Summary of Contact: Advised Charlie that Don Willet of ANDROS will probably call him shortly to arrange an appointment for the week of December 4th. ANDROS would like to deliver a proposal for an early warning fire detection system based on their CO monitor and would like to demonstrate the CO monitor at that time.
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (Cont'd)

Date: 11/20/72
Type of Contact: Correspondence
Person Contacted: Todd Anuskiewicz
GWU
2001 S. Street N. W.
Washington, D. C. 20009
By: R. P. Donovan

Summary of Contact: Sent Todd a list of Arkon contracts leading to the development of their CO monitor plus some background information on the patent status. Also included a reprint from November R/D magazine, "Infrared Fluorescence Analysis", F. W. Karasek, P. 36-37 (See Appendix B). cc: Don Willett, Charles Eastwood. (Appendix B)

C. RTI/AP-48, Modifications to Mass Spectrometry to Enhance Its Performance in Air Pollution Monitoring

Date: 11/3/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Conrad S. Josias, President
Analog Technology Corp.
3410 East Foothill Blvd.
Pasadena, Cal. 91107

Summary of Contact: Mr. Josias expressed ATC interest in developing a mass spectrometer - most likely a tandem quadruple - that could meet the requirements for an ambient air monitor as well as those of a breath analyzer for trace contaminants buildup in the alveolar air of various industrial workers (See Appendix C). He included also: (1) Excerpts from ATC's proposed Sub Atmosphere Analyzer; (2) Residual Gas Analyzer Proposed (to MSFC); and (3) A brochure describing a commercially available Respiratory Gas Analyzer (based on NASA technology).

Date: 11/9/72
Type of Contact: Telephone
Person Contacted: George Wood
NASA IRD
LRC

By: R. P. Donovan

Summary of Contact: No further action yet - George expects to visit Ruben during Nov. I'll check with him after Thanksgiving if I haven't heard from him.

Told George of Analog Technology Corp.'s interest. George told me of AVCO Tulsa's interest in modifying the cycloidal mass spect.
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (Cont'd)

Date: 11/20/72
Type of Contact: Telephone
Person Contacted: Charlie Eastwood
By: R. P. Donovan

Summary of Contact: Charlie told me that a Neal Johnson from Spectra Systems had visited him on Friday to promote a mass spectrometer concept that Bob Stevens of EPA would endorse. Charlie suggested a proposal to TU that would both satisfy Stevens and Cleveland would be optimum - Johnson will call Ayer or me.

Date: 11/27/72
Type of Contact: Telephone
Person Contacted: F. A. Ayer; R. P. Donovan
By: Neal Johnson
Spectra Systems
3001 Red Hill Avenue
Bldg. 1-107
Costa Mesa, California 92624
(714) 979-3400

Summary of Contact: Neal called to describe a re-engineering/repackaging of a NASA LRC mass spectrometer for air pollution applications.

The instrument he described is a combination chromatograph-mass spectrometer. It utilizes an absorption column to achieve a high sensitivity (he mentioned parts per trillion for some species) and a high dynamic range. The repackaging effort he proposed is one which would result in a small portable instrument, about the size of a suitcase, which would be capable of unattended operation for up to 30 days and would hopefully cost less than $10,000 in commercial production.

Neal said that Bob Stevens of EPA had reacted very favorably to the idea and would no doubt be an enthusiastic endorser of the development from EPA's viewpoint.

I promised to mail Neal a copy of our mass spectrometer specification and encouraged him to respond by submitting a proposal to TU and to us for this development.

Date: 11/27/72
Type of Contact: Correspondence
Person Contacted: Neal Johnson, Spectra Systems
By: R. P. Donovan

Summary of Contact: Mailed Neal Johnson a copy of the mass spectrometer specification.
I. Contacts Made on Environmental Problems (Cont'd)

D. RTI/AP-61, Mathematical Model for Prediction of Pollutant Formation During Combustion

Date: 11/30/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: MS451
NASA LERC


E. RTI/AP-71, Instrumental Methods for Analysis of Formaldehyde in Ambient Air and Auto Exhaust

Date: 11/1/72
Type of Contact: Telephone
Person Contacted: Dr. Larry Hrubesh
LLL
Univ. of Cal.
By: R. P. Donovan

Summary of Contact: Requested to be placed on the distribution list for the quarterly progress reports being generated under the joint EPA/NASA formaldehyde detector instrument development. Larry agreed to do so and said he would mail me a copy of the first which was sent out about two weeks ago.

The program is off to a good start. Big problem has been the inadequacy of the commercial membranes they hoped to use on the input - seems they contain small holes. This problem is not yet solved, although a European manufacturer is reported to have a better product. This will be checked out but they may find themselves in the membrane development business.

Date: 11/6/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Dr. L.W. Hrubesh

Summary of Contact: Received a copy of the Quarterly Report entitled "Feasibility Study of a Gunn Diode Microwave Cavity Spectrometer as a Formaldehyde Gas Monitor", June-August 1972, EPA-IAG-D179 (D)/NASA-L-75902, 19 September 1972. (See Appendix D.)
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (Cont'd)

F. RTI/OC-16, Measurement of the Osmo-Regulation of Blue Crab

Date: 11/1/72
Type of Contact: Correspondence
Person Contacted: Todd Anuskiewicz
GWU
By: F. A. Ayer

Summary of Contact: Sent Todd a letter that recommended that NASA support Dr. Dave Engel's work at the Atlantic Estuarine Fisheries Center. (Appendix E)

Date: 11/2/72
Type of Contact: Telephone
Person Contacted: Dave Engel
By: F. A. Ayer

Summary of Contact: Returned Dave's call. He thought the letter to Todd Anuskiewicz and the enclosure entitled "Technology Transfer Potential of the Blue Crab Monitor" was excellent and described his program very well. (Appendix E)

He suggested that the next to last paragraph be changed to read: Dr. T. R. Rice, Director of the Atlantic Estuarine Fisheries Center has indicated that if hiring practices and support is available that the assignment of a technician to the task of gathering these data under the supervision of Dr. Engel would be made. The possibility exists of assigning even still another technician, should the program warrant it.

He also stated that his presentation at the University of South Carolina to the Comparative Biochemistry and Physiology Section of American Society of Zoologists, Oct. 26-28, was very well received. Apparently, a number of attendees indicated they planned to write RTI or LRC for further information.

In addition, Dave said that a photographer from the National Geographic was down this week to take some more pictures.

Date: 11/3/72
Type of Contact: Correspondence
Person Contacted: John Samos
NASA LRC
By: R.P. Donovan

Summary of Contact: Mailed John a copy of Frank Ayer's letter to Todd Anuskiewicz including the recommendation for further NASA support of the blue crab research (See Appendix E).
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

I. Contacts Made on Environmental Problems (Cont'd)

Date: 11/3/72
Type of Contact: Telephone
Person Contacted: Todd Anuskiewicz
By: F. A. Ayer

Summary of Contact: Called Todd and told him about the changes to the letter I sent him on 1 November.

Monitoring Parameters of Estuarine Waters

Date: 11/2/72
Type of Contact: Telephone
Person Contacted: F. A. Ayer
By: Charles Hussin, LRC

Summary of Contact: Charlie called and wanted to know who was interested in this problem. I told him that Dr. Engel at the Atlantic Estuarine and Fisheries Center was certainly one. Also told him that EPA and NOAA would probably be very interested if a solution could be suggested.

Mentioned to Charlie that our trip to see Dr. Engel about his Blue Crab experiments was very successful.
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources

A. FCP-3, Develop a Technique for Measuring the Size and Concentration of Particulates

Date: 11/2/72
Type of Contact: Telephone
Person Contacted: Dr. George Carson, NIOSH
By: R. P. Donovan

Summary of Contact: Checked status of NIOSH support of FCP-3. It's in procurement - a 10 point plan being prepared within the next week or two. George estimated that NASA should be hearing something before December 1st.

Date: 11/6/72
Type of Contact: Telephone
Person Contacted: F. A. Ayer
By: Charles Eastwood, TUO NASA

Summary of Contact: Charlie called and said that Dr. Carson, NIOSH, had come in with his letters proposing that they joint fund up to $5,000.00 with NASA on the FCP-3 problem. Charlie will be at LRC on Thursday and will talk to Staylor about what can be done to get this problem manned and funded.

Date: 11/13/72
Type of Contact: Telephone
Person Contacted: Charlie Eastwood
   - NASA Headquarters
   Telephone: (202) 755-3855
By: R. P. Donovan

Summary of Contact: Dr. Carson has committed NIOSH in writing to 5K for FCP-3. Staylor can't perform because his team has been broken up. Charlie recommended: (1) Review of coal dust monitor by Carson; (2) Frank exchange between Carson and Staylor on whether to proceed.

I'll take the lead in bringing this about and will check with O'Keefe and Thompson regarding their evaluation of the Lewis techniques on cobalt and nickel analysis.

Date: 11/16/72
Type of Contact: Telephone
Person Contacted: Serge Ucetta
   - IITRI TATeam
By: J. M. Brown
II. Contacts Made on NASA Field Center Proposals and Proposals
Received from Other Sources (Cont'd)

Summary of Contact: I contacted Uccetta to obtain technical information on ERC developed particulate monitor and status of IITRI's efforts to transfer this technology to an application as a coal dust monitor. Serge indicated he will send technical report to determine status of any continuing development activity involving the monitor. Apparently, the Bureau of Mines was not receptive to this technology when it was demonstrated to them approximately 18 months ago.

Date: 11/16/72
Type of Contact: Telephone
Person Contacted: Mr. Dick Miner
NASA, TUD

By: J. M. Brown

Summary of Contact: Dick indicated that work on the ERC particulate monitor was still underway at TSC (Transportation Systems Center) and that we should contact Dr. William Levitt for status and further technical information. Dick also stated that the primary reason that the Bureau of Mines was not interested in the ERC monitor was that the monitor is not specific for coal dust; it responds to all particulates.

Date: 11/18/72
Type of Contact: Telephone
Person Contacted: Dr. William Levitt
Transportation Systems Center

By: J. M. Brown

Summary of Contact: The most important result of my conversation with Levitt is that the ERC particulate monitor which was developed for Apollo missions is no better than commercially available particulate monitors in any way except that it is flight hardware.

Date: 11/20/72
Type of Contact: Telephone
Person Contacted: Mr. Charles Eastwood
NASA TUD

By: James M. Brown

Summary of Contact: I informed Charlie that the ERC-developed particulate monitor offered no technical advantage over commercial instruments and that, as a result, our best opportunity for solving NIOSH's requirements is to continue to attempt to initiate the re-engineering project proposed by Langley Research
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Center and involving a new approach to particulate size and concentration monitoring. We agreed that the next step is to set up direct communications between George at NIOSH and Frank Taylor at ERC in order to insure that NIOSH's requirements and the potential in LRC's approach are compatible. RTI is proceeding to set up this direct exchange.

B. FCP-4, Character of Aerosols in the Atmosphere

Date: 11/1/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: John Samos
TUO LRC

Summary of Contact: Received, from John, the monthly status report on FCP-4.

Date: 11/27/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: ISOMET
103 Bauer Drive
Oakland, N.J. 07436
(201) 337-3811

Summary of Contact: Received a News Release entitled "ISOMET Develops Electronically Tunable Optical Filter", March 27, 1972, plus other product literature.

Date: 11/27/72
Type of Contact: Correspondence
Person Contacted: Dr. S.H. Melfi
NASA LRC
By: R. P. Donovan

Summary of Contact: Mailed Harvey a copy of the ISOMET News Release of 3/27/72, entitled "ISOMET Develops Electronically Tunable Optical Filter".
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Date: 11/28/72  
Type of Contact: Telephone  
Person Contacted: R. P. Donovan  
By: Dr. Pat McCormick  
NASA LRC

Summary of Contact: Pat called at the suggestion of Charlie Eastwood to ask our assistance in setting up an EPA visit for him, Bill Holton, Franklin Harris possibly to describe their LIDAR work and particle sampling in California. The LRC researchers are interested in guidance for future activities and possibly in associating with the St. Louis experiment of next fall.

I agreed to attempt to arrange appointments with Dr. Bob McCormick, Dr. William Wilson and Mr. John Nader.

Date: 11/28/72  
Type of Contact: Telephone  
Person Contacted: Dr. Bob McCormick  
EPA  
Div. of Meteorology  
549-8411, 4541  
By: R. P. Donovan

Summary of Contact: McCormick said that Dr. Warren Johnson, his Chief of Research, would be the person for the LRC people to talk to. Johnson is from the SRI LIDAR team, is now with NOAA, assigned to EPA. He heads the St. Louis experiment and has an SRI LIDAR to take there.

McCormick said that Johnson would be in all day tomorrow and that the EPA–NASA LIDAR exchange should be through him.

Date: 11/28/72  
Type of Contact: Telephone  
Person Contacted: Dr. Pat McCormick  
NASA LRC  
By: R. P. Donovan

Summary of Contact: I told Pat of Bob McCormick's (EPA) suggestion to work through Warren Johnson. Johnson will be gone Thursday and Friday of this week but will be in all day tomorrow. Pat agreed to make his trip contingent upon Johnson's availability which means Tuesday (Dec. 5), Thursday (Dec. 7) or Friday (Dec. 8) of next week. Once Johnson is lined up, then Wilson and Nader can be brought in.

I agreed to call Pat again tomorrow with the word from Johnson.
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Date: 11/29/72
Type of Contact: Telephone
Person Contacted: Colleen Peterson
EPA
(Dr. Wilson's secretary)
549-8411, X2181
By: R. P. Donovan

Summary of Contact: Left a message for Dr. Wilson that Pat McCormick would be at EPA on Tuesday, December 12 and would like to arrange a time if he's available. Colleen said she'd relay the message and ask Wilson to call back.

Date: 11/29/72
Type of Contact: Telephone
Person Contacted: R. P. Donovan
By: Dr. William Wilson

Summary of Contact: Wilson has meeting scheduled for December 12, but he said he would like to talk with Pat McCormick et al. He recommended a call in the PM before coming over.

He said somebody from the NASA LRC LIDAR was in last month talking about a joint funded program; he thought it was McCormick but wasn't sure.

Date: 11/29/72
Type of Contact: Telephone
Person Contacted: Dr. Warren Johnson
Div. Meteorology
EPA
RTP - NERC
549-8411, X4565
By: R. P. Donovan

Summary of Contact: Arranged a 9:00 a.m., Tuesday, December 12, East Side, meeting with Johnson for Pat McCormick's LRC LIDAR team. Warren said he knew McCormick, was in the California experiment with a LIDAR about the same time and would like to host the visit. He also said he might "put on a show" with his own LIDAR in the parking lot.

Date: 11/29/72
Type of Contact: Telephone
Person Contacted: Dick Story
NASA LRC
(703) 827-3532
By: R. P. Donovan
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Summary of Contact: Told Dick of the arrangements: 9:00 a.m., December 12, Dr. W. Johnson; p.m., December 12, Dr. W. Wilson. Dick said Pat McCormick was out sick but he would relay the message. The travel party has swelled to 4 or 5 now; they will have to make it a one-day journey because of travel limitations which means a 4-5 a.m. departure.

C. FCP-9, Remote Measurement of Particle Numbers and Size Distribution for Monitoring Smokestack Emissions

FCP-10, Remote Instrument for Measurement of Exhaust Emission Flow Rate

Date: 11/1/72
Type of Contact: Correspondence
Person Contacted: John S. Nader
EPA
RTP - NERC

By: R. P. Donovan

Summary of Contact: Mailed John a news release (Electro-Optical Systems Design, October 72, p. 11) on Huffaker's doppler laser system operating from the Ames Convair 990. Also reminded John of our interest in receiving his evaluation of FCP-9,10.

Date: 11/9/72
Type of Contact: Telephone
Person Contacted: John Nader
EPA
RTP - NERC
919-549-8411 ex2381

By: R. P. Donovan

Summary of Contact: Checked on status of EPA review of FCP-9,10. John said Bill Herget was out all week, but he assumed that the review was either done and sent in or about to be. He gave me Bill's number (X2216) and suggested I check with him directly next week.
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Date: 11/16/72  
Type of Contact: Telephone  
Person Contacted: Bill Herget  
EPA  
RTP-NERC  
919-549-8411 X2216  
By: R. P. Donovan

Summary of Contact: Bill has finished his review and forwarded it to John Nader (two days ago). Both Headquarters and RTI should receive copies of this endorsement within a week. Bill said he was quite positive about the NASA proposals and felt they complemented EPA's own work at Tullahoma. His letter is one of endorsement.

Date: 11/21/72  
Type of Contact: Correspondence  
Person Contacted: R. P. Donovan  
By: Bill Herget  
EPA  
RTP - NERC  
RTP, N. C.  

Summary of Contact: Received copy of endorsing statement on FCP-9,10 mailed to Jeff Hamilton by Bill. (See Appendix F).

Date: 11/21/72  
Type of Contact: Correspondence  
Person Contacted: Milton Huffaker  
MSFC  
By: R. P. Donovan

Summary of Contact: Mailed copy of Bill Herget's endorsement to Milton.

D. FCP-16, Forest Fire Detection and Location

Date: 11/13/72  
Type of Contact: Telephone  
Person Contacted: R. P. Donovan  
By: David Winslow  
MSFC TU
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Summary of Contact: Changes in firefighting in Alabama:
(1) Original proposal is out of date (one that Frank Ayer sent to Alabama); (2) TU men cannot work on projects (Winslow is out); (3) Astrionics wants to work on Video scanning approach; (4) NASA can no longer participate in hardware development; (5) Copy of new proposal is on way to F. A.; (6) System analysis is the role of NASA including displays, microwave link. They're considering a vertically mounted t.v. camera with: (1) Dove prism - rotates and reconverts normally inverted image (2) Conical mirror - gives display like a PPI scope. Filters, IR images are also to be considered; they plan to evaluate microwave link vs. hardware coupling. No longer will hardware be delivered to Alabama Forestry Commission but just the development of an overall fire spotting system.

Dave also agreed to mail updated package on FCP-12. This proposal was originally for a Zinc O₂ battery but is now realized to be no good because of Zinc migration. Cd-O₂ is better battery but far too expensive. The Eagle Pilcher Co. has looked at Pb-O₂ which is three times as efficient as Pb-acid. In addition, it is completely sealed and, therefore, useful in an explosive atmosphere or under water. It features an easy quasi-mechanical recharge and is now the preferred system.

Dave also plans to mail a request for advice on air pollution monitors that could be mounted on a buoy.

Date: 11/17/72
Type of Contact: Correspondence
Person Contacted: David Winslow
TU MSFC
By: F. A. Ayer

Summary of Contact: Received draft copy of a proposal for Forest Fire Detection and Location.

Date: 11/27/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Charles Eastwood
TUO, NASA Hdqtrs.

Summary of Contact: Received, from Charlie, the updated proposal from MSFC for FCP-16, Forest Fire Detection System.
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Date: 11/29/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Charles Eastwood
    NASA Headquarters

Summary of Contact: Received from Charlie a copy of a letter that he sent to Marvin Brown in regards to MSFC's up-dated Forest Fire Detection and Location System proposal. Attached to the letter was a copy of Marvin Brown's letter to Jeff Hamilton and a copy of MSFC's up-dated proposal (See Appendix G).

Date: 11/29/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: H. C. Lucas
    Forest Resource Protection Div.
    Alabama Forestry Commission
    513 Madison Avenue
    Montgomery, Alabama 36104

Summary of Contact: Received from Mr. Lucas a letter indicating support by the Alabama Forestry Commission for the development of a remote forest fire detection system (See Appendix H).

Date: 11/29/72
Type of Contact: Correspondence
Person Contacted: Mr. H. C. Lucas
By: F. A. Ayer
    Forest Resource Protection Div.
    Alabama Forestry Commission
    513 Madison Avenue
    Montgomery, Alabama 36104

Summary of Contact: Acknowledged receipt of Mr. Lucas' letter dated 22 November and forwarded to him MSFC's up-dated proposal for his review. (Appendix G, I).

E. FCP-17, California Aerosol Study

Date: 11/1/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: John Samos
    TUU LRC
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Summary of Contact: Received from John the monthly status report on FCP-17.

F. FCP-18, University of Missouri Study

Date: 11/20/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Brad Evans
AMES

Summary of Contact: Received October monthly status report.

Date: 11/21/72
Type of Contact: Correspondence
Person Contacted: Bob Stevens
EPA
RTP - NERC
By: R. P. Donovan

Summary of Contact: Mailed copy of the Project Status Reports (10/31/72) on FCP-18.

G. FCP-19, Martin-Marietta Study

Date: 11/20/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Brad Evans
AMES

Summary of Contact: Received October monthly status report.

Date: 11/21/72
Type of Contact: Correspondence
Person Contacted: Bob Stevens
EPA
By: R. P. Donovan

Summary of Contact: Mailed Bob a copy of the Project Status Report (10/31/72) on FCP-19.
II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

H. FCP-20, Colorado State University Study

Date: 11/3/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Dr. Francis Pooler, Jr.
EPA
RTF - NERC

Summary of Contact: Received a critique of the Acoustic Radar Proposal from Colorado State University. Generally a low rating because of insufficient detail. (See Appendix J).

Date: 11/3/72
Type of Contact: Correspondence
Person Contacted: Dr. Roger Vickers
CSU
Ft. Collins, Colorado 80521
By: R. P. Donovan

Summary of Contact: Mailed Roger a copy of Dr. Pooler's Comments on the CSU Acoustic radar proposal. (Appendix J).

Date: 11/13/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Dr. Roger Vickers
Assoc. Prof. of E. E.
Colorado State Univ.
Ft. Collins, Colorado 80521

Summary of Contact: Roger responded to my letter containing Dr. Pooler's criticisms of his proposal. Roger has called Pooler whose "position may have changed from that stated in his letter." Roger said he'd be happy to provide additional proposal type details on request and re-iterated his claim that his proposed research was an "interesting case of technology utilization, with immediate application to the pollution assessment problem and to local weather mapping."

Date: 11/13/72
Type of Contact: Telephone
Person Contacted: R. P. Donovan
By: Charlie Eastwood
NASA Hqtrs.
(202) 755-3855
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

II. Contacts Made on NASA Field Center Proposals and Proposals Received from Other Sources (Cont'd)

Date: 11/13/72
Type of Contact: Telephone
Person Contacted: Charlie Eastwood
               NASA Hqtrs.
               (202) 755-3855
By: R. P. Donovan

Summary of Contact: Charlie encouraged new proposal from the Colorado State University group with the idea of joint EPA-NOAA/NASA sponsorship. He also encouraged response from Analog Technology.

Date: 11/17/72
Type of Contact: Correspondence
Person Contacted: Dr. Roger Vickers
                 Colorado State University
By: R. P. Donovan

Summary of Contact: Suggested that Roger prepare a new acoustic radar proposal for NASA TU. This proposal will be reviewed probably by both EPA and NOAA. Joint funding between NASA TU and one of these agencies is the support mode being sought. CC of letter sent to Dr. Francis Pooler, EPA, Brad Evans, Ames R. C., and Charles Eastwood, NASA Hqtrs.

Date: 11/27/72
Type of Contact: Telephone
Person Contacted: R. P. Donovan
By: Dr. Roger Vickers

Summary of Contact: Roger called to confirm his intention to submit a new Proposal on acoustic radar. He plans to coordinate with Freeman Hall of Dr. Little's group at Boulder so as to be responsive to their needs as well as those of EPA.

I recommended he submit his proposal to Charles Eastwood with copies going to Brad Evans at Ames and to me at RTI.
III. Contacts with NASA Headquarters, Field Centers, George Washington University, and Other Organizations that are not related to a specific environmental problem or proposal

A. Contacts with NASA Headquarters

Date: 11/8/72
Type of Contact: Telephone
Person Contacted: Charles Eastwood
By: F. A. Ayer

Summary of Contact: Discussed with Charlie points he had discussed with Bob Donovan the day before (FCP-3, RTI/OC-16, etc).

Date: 11/20/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Charles Eastwood/KT

Summary of Contact: Received memo, "A Rapid Procedure for Determination of Nickel, Cobalt and Chromium in Airborne Particulate Samples" by Warren F. Davis and Judson W. Graab. He also included their FTS number. This information is to go to Dick Thompson at EPA. (Appendix K).

Date: 11/21/72
Type of Contact: Correspondence
Person Contacted: Charles Eastwood
By: F. A. Ayer


Date: 11/22/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Todd Anuskiewicz

GWU
ENVIRONMENTAL TECHNOLOGY APPLICATION TEAM CONTACTS

III. Contacts with NASA Headquarters, Field Centers, George Washington University, and Other Organizations that are not related to a specific environmental problem or proposal (Cont'd)

Summary of Contact: Received, from Todd, the following articles: "Potential Applications of NASA-Developed Technology to Problems of the Environment" by L. W. Ross and J. N. Pecoraro, ASME Publication 72-ENAv-23.


Date: 11/27/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Charles Eastwood
TUO NASA Hqtrs.

Summary of Contact: Received a brochure on Spectra Systems.

B. Contacts with Field Centers

Date: 11/20/72
Type of Contact: Correspondence
Person Contacted: F. A. Ayer
By: Sandy Kocsis
Lewis Research Center

Summary of Contact: Received a request to update RTI's NASA Technology Utilization Program Roster. Forwarded information to her.

C. Contacts with Other Organizations

Date: 11/2/72
Type of Contact: Correspondence
Person Contacted: R. P. Donovan
By: Len Sauer
JPL
III. Contacts with NASA Headquarters, Field Centers, George Washington University, and Other Organizations that are not related to a specific environmental problem or proposal (Cont'd)

Summary of Contact: No formal documentation available on Tech Brief 72-10072 which was carried out with local air pollution people by JPL workers on their own time.

Date: 11/2/72
Type of Contact: Telephone
Person Contacted: M. Torgenson
SRI TATeam
By: R. P. Donovan

Summary of Contact: Recommended LIDAR as a potential solution to Diesel Plume measurement. Offered to help promote any EPA/AAR interchange that seems appropriate.

Date: 11/15/72
Type of Contact: Telephone
Person Contacted: Dr. Dick Thompson
EPA
RTP – NERC
(919) 549-8411 X2454
By: R. P. Donovan

Summary of Contact: Dick said that he had a "latent" interest in the suggestion of Graab and Davis as discussed in their article "A Rapid Procedure for Determination of Nickel, Cobalt, and Chromium in Airborne Particulate Samples" from LERC. He regarded it as new and worthwhile but had not yet had either the time or the manpower to follow up. He requested that I furnish the FTS numbers of Davis and Graab along with two additional copies of the memo (see Contact, p. 25, September Monthly Report, and Appendix K.).

Date: 11/20/72
Type of Contact: Correspondence
Person Contacted: Dr. Dick Thompson
EPA
By: R. P. Donovan

Summary of Contact: Mailed Dick Thompson the NASA LeRC memo received from Charles Eastwood. (Appendix K)
APPENDIX A

LETTER FROM DON WILLET, ANDROS, TO ROBERT DONOVAN, RTI

27 OCTOBER 1972 WITH THE FOLLOWING ATTACHMENTS:

* LIST OF ADVERTISEMENTS


* REPRINT FROM THOMAS REGISTER WITH PRODUCT LISTING

* PREPRINT OF AN ARTICLE ENTITLED "THE FLUORESCENT CO ANALYZER" F. W. KARASEK, R&D, NOV. 1972.

* ANDROS BROCHURE
October 27, 1972

Mr. Robert Donovan
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park
North Carolina 27711

Dear Bob:

As you requested, here is a pile of information relating to the marketing of the Andros 7000 CO Analyzer. One of the impressive items which is missing by necessity is the article that will appear in the November issue of R/D magazine. For your information, I have included the draft of this article. I wish some of this information was more aesthetically pleasing, but it's all we have.

Here's a list of the companies and agencies who have purchased (or will soon purchase) the Andros 7000 and the application for which they will be used:

<table>
<thead>
<tr>
<th>Customer</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meteorology Research Inc. (2)</td>
<td>Airborne air monitoring</td>
</tr>
<tr>
<td>Bureau of Mines</td>
<td>Personnel safety in mines</td>
</tr>
<tr>
<td>Olson Laboratories</td>
<td>Calibration of low-level span gas.</td>
</tr>
<tr>
<td>Stanford University</td>
<td>Endogenous production of CO in infants.</td>
</tr>
<tr>
<td>EPA - Ann Arbor</td>
<td>Automotive emissions</td>
</tr>
<tr>
<td>NASA - Lewis</td>
<td>Aircraft emissions</td>
</tr>
<tr>
<td>Canadian DOE (2)</td>
<td>Ambient air monitoring,</td>
</tr>
<tr>
<td>Koritsu (Japan)</td>
<td>Ambient air monitoring,</td>
</tr>
<tr>
<td>Western Electric</td>
<td>Industrial Hygiene (OSHA)</td>
</tr>
<tr>
<td>Bureau of Mines</td>
<td>Early-Warning fire detection.</td>
</tr>
<tr>
<td>Naval Research Lab (2)</td>
<td>Personnel safety in submarines.</td>
</tr>
<tr>
<td>EPA - RTP</td>
<td>Ambient air monitoring.</td>
</tr>
<tr>
<td>UC - Riverside</td>
<td>Mobile ambient air monitoring.</td>
</tr>
<tr>
<td>California ARB - LA</td>
<td>Airborne air monitoring.</td>
</tr>
<tr>
<td>California ARB - Sac.</td>
<td>Ambient air monitoring.</td>
</tr>
<tr>
<td>Yuma Proving Grounds (Army)</td>
<td>CO emissions from airborne armament.</td>
</tr>
<tr>
<td>Various others</td>
<td>Ambient air monitoring.</td>
</tr>
</tbody>
</table>

26
Bob, I hope this information will be helpful to you. Let me know if we can do anything else.

Best regards,

Don Willett
Director of Marketing
A new "dual-isotope-fluorescence" technique, for industrial health and safety monitoring of ambient carbon monoxide levels, achieves high specificity and sensitivity by using energy fluoresced from excited CO gas molecules as its sensing beam. The solid-state instrument is unaffected by shock and vibration (unlike conventional infrared instruments, says the manufacturer), and can be operated with accuracies better than 1 ppm. by nontechnical personnel.—Andros, Inc., Berkeley.
Carbon monoxide analyzer uses principle of gas fluorescence for accurate measurement.

Carbon Monoxide Analyzer
Measures Changes Less Than 0.2 ppm

High accuracy with high specificity—immunity to particles, water vapor or non-CO gases—are featured in a carbon monoxide analyzer. Designated Model 7000 by Andros, Inc., the instrument determines CO concentration to less than 0.2 ppm by measuring absorption of a characteristic spectrum of infrared radiation.

Previous limitations of the technique are said to be solved by using radiation actually fluoresced from excited CO gas molecules in the sensing beam. Two isotopes of CO are used in the device and a sequential IR filtering scheme uses them as a reference to provide stability. Contact Andros or circle 306 on Reader Service Card.

INQ. TO DATE: 39

R&D July, 1972

Carbon monoxide analyzer has 0.2 ppm sensitivity

Using dual-isotope fluorescence, Andros 7000 carbon monoxide analyzer from Andros Inc., Berkeley, Calif., operates from 32 to 122 F. With sensitivity to 0.2 ppm, instrument is available in 20, 50, 100 and 200 ppm ranges. Accuracy is 1 per cent of reading ± 1 per cent of full scale. Circle 399 on Reader Card.

INQ. TO DATE: 29
CO ANALYZER
for industrial safety monitoring
ANDROS 7000 is an atmospheric carbon monoxide analyzer designed for industrial health and safety monitoring. It incorporates a dual-isotope-fluorescence sensing technique which makes the instrument stable, insensitive to shock and vibration and easy to operate. ANDROS 7000 can be operated by non-technical personnel and even mounted on an in-plant vehicle for roving inspection programs. Instrument determines the concentration of CO in plant atmosphere with better than 1 ppm accuracy by measuring absorption of a characteristic spectrum of IR radiation. Instrument achieves specificity and sensitivity by using energy actually fluoresced from excited CO gas molecules as the sensing beam. As this radiation is at the specific wavelength absorbed by CO, the instrument is inherently specific to that gas. Andros, Inc.
Pollution Instrumentation: A Trend toward Physical Methods

Air pollution has largely ended the battle of legislative restriction, particularly the Clean Air Act of 1970, has enacted to define permissible concentrations of pollutants in emissions from key sources and to establish acute levels of air pollutants for states, cities, and areas. The principal instruments are the development of more refined technologies to limit pollutants and the enforcement of the standards. Implicit in each of these is the need for suitable means to measure pollutant concentrations.

Production of air pollution instrumentation is a rapidly growing, ill-defined, and surprisingly complex sphere that is attracting a sufficient number of companies, including new ones, to move into two classes: those for measuring concentrations of pollutants, and those for determining their presence. The major disadvantages include the limited number of pollutants to which the techniques are sensitive, the high initial expense for the instruments, maintenance of the instrument, and new ones are appearing regularly. These instruments have two common characteristics: few have received sufficient testing by EPA and independent laboratories to ensure their accuracy and reliability, and most will undoubtedly become obsolete before the end of the decade. For perhaps the single clearest trend within this field is a growing shift away from the complexity of chemical techniques and toward the simplicity of physical methods of measurement that monitor many pollutants simultaneously.

The most widely used instruments, currently, however, are based on wet chemical techniques, which were among the first to be developed and whose capabilities are thus most clearly defined by experimental data. Such instruments generally depend on colorimetric, coulometric, or conductimetric procedures to measure the concentration of a pollutant in a collection liquid through which the sample has been passed. In the standard reference method for nitrogen dioxide, for example, the gaseous sample is bubbled through a solution of sodium hydroxide, where the NO₂ is converted to stable sodium nitrate. After collection, the nitrate is diazotized with phosphoric acid sulfanilamide and coupled to N-1-naphthyl ethylenediamine; the concentration of the resulting chromophore is then determined colorimetrically.

Many Problems with Wet Chemicals

Wet chemical techniques readily lend themselves to automation and yield highly reproducible results. They are also sensitive, simple to operate, and inexpensive. These advantages are, however, largely offset by many drawbacks, including interference by other pollutants, instability of reagents, generation problems associated with the complicated plumbing required, the need for different reagents for each species monitored, and the amount of time required for sampling and quantification.

Further problems arise in sampling. Earlier this summer, for example, EPA deputy administrator Robert W. Fri disclosed that average NO₂ concentrations determined in several areas of the United States were erroneous because of simpler assumption of collection efficiency. Using newly developed devices to generate known concentrations of NO₂, EPA investigators found that the collection efficiency of NO₂ in sodium hydroxide varies with the concentration of NO₂ in the sample. The collection efficiency is less than 15 percent at NO₂ concentrations greater than 300 parts per billion (ppb), about 35 percent at concentrations near 60 ppb, and rises to at least 60 percent at concentrations less than 25 ppb; EPA had previously assumed that the efficiency was constant. It is, of course, possible to establish a calibration curve for sampling efficiency, but sharp fluctuations of NO₂ concentration during the sampling period make accurate calculation of the average concentration exceptionally difficult, if not impossible.

Wet chemical techniques are thus losing favor with environmental scientists, notes Alfred Ellison of EPA's division of chemistry and physics, although the relatively low cost of such instruments ensures their continued use. Many users, he adds, are now switching to instruments based on chemical techniques as chemiluminescence, electrochemical transducers, and flame ionization coupled with gas chromatography.

Chemiluminescence has many advantages in comparison to wet chemical techniques, and is now the standard reference method for measuring NO₂ concentrations. The technique is sensitive and specific, and measurements are rapid and highly reproducible. The major disadvantages include the relatively large initial expense for the instrument, maintenance of the plumbing and the gaseous reagent, and the limited number of pollutants to which the technique is applicable.
Electrochemical transducers would appear to represent a significant advance in pollutant detection. These devices depend on selective electrocatalytic oxidation (or reduction) of the pollutant in a cell that is very similar to a fuel cell. In a typical transducer, the sample gas flows past a semipermeable membrane that allows a small, constant fraction to enter the cell. Inside the cell, the sample diffuses through a thin liquid film to an electrocatalytic electrode, where a charge transfer reaction occurs. Basic electrolyte and a reference electrode make up the rest of the cell. In operation, the cell produces an electrical potential that is directly proportional to the concentration of pollutant in the sample stream and, within reasonable limits, is independent of the sample flow rate.

Such transducers have a number of advantages, including low cost, ease of maintenance, simplicity of operation, and versatility. Several inexpensive cells, each specific for a different pollutant, can be linked to one instrument that contains the electronics assembly, thus providing multipollutant capability. Many problems are associated with their use, however.

Recent industrial tests, says Craig Hollowell of the environmental instrumentation group at Lawrence Berkeley Laboratory, indicate that problems of baseline drift and interference by other pollutants are greater with transducers than with any other type of commercial instrument. Other problems he cites include insufficient instrument stability, evaporation of the electrolyte, and reduced cell lifetimes caused by clogging of the membrane in heavily polluted samples (although cells can be rejuvenated by the manufacturer). The low price of transducers makes them very popular for source monitoring applications, Hollowell points out, but without further refinements they will probably remain no more than a stopgap technique.

Gas chromatography is being used increasingly for pollutant monitoring because of its ability to separate similar pollutants before their concentrations are measured. Such a procedure is especially important in the measurement of hydrocarbon concentrations: Federal standards establish maximum concentrations for all hydrocarbons except methane, which is generally considered innocuous and is thus left uncontrolled. Hydrocarbon monitoring techniques must therefore be able to exclude methane or to measure its concentration independently, and gas chromatography fills this need perfectly.

In a typical installation, the chromatograph separates methane, carbon monoxide, and other hydrocarbons. The concentration of each is then generally determined with a flame-ionization detector, in which the pollutant is burned in a hydrogen-rich flame. The method is sensitive, rapid, and highly specific, and has now been adapted for monitoring sulfur-containing pollutants.

**Chromatographs Highly Automated**

Modern air pollution chromatographs are highly automated instruments capable of unattended operation for extended periods, according to Larry Dvoretsky of the reentry and environmental systems division of General Electric Company, Philadelphia, Pennsylvania. General Electric is thus using both sulfur and hydrocarbon chromatographs in a statewide pollution monitoring system that it is designing for Pennsylvania. An additional advantage of these instruments, he adds, is that they frequently can indicate the existence of pollutants whose presence is unknown or unexpected.

But gas chromatographs also have several drawbacks, points out Franz J. Burman of EPA's air surveillance branch. They require extensive maintenance, he says, and their operators generally have to be technically trained. Other shortcomings include the need for a constant supply of carrier gas, the cycling time associated with operation of the chromatograph, and the length of time required for stabilization of the column when the instrument is turned on.

The general complexity of all the previously mentioned systems, the necessity for handling reagents, and the general lack of multipollutant capability are among the many factors mediating a growing trend toward physical methods of measurement. Environmental scientists, says EPA's Ellison, are now in the early stages of an extensive shift to optical detectors based on infrared or ultraviolet spectroscopy. Only a few such instruments are on the market now, notes Berkeley's Hollowell, but the number seems certain to grow as newly developed improvements are incorporated.

Such improvements are necessary to overcome many of the problems that have hindered the development of optical techniques for pollutant monitoring. Foremost among the problems is that of interference from other pollutants and, particularly, water vapor—a problem most often manifested as an inability to provide a suitable reference against which the sample can be compared. Others include susceptibility of the optics to vibrations, long-term instability of the associated electronics, and condensation of pollutants on the optics. Counterbalancing these problems, however, are high sensitivity, simplicity, portability, speed of measurement, and their potential for detecting many pollutants.

Optical techniques can be divided into two broad categories: nondispersive instruments, which transmit the complete spectrum through the sample and modify the detector for selectivity, and dispersive instruments, in which a prism or grating is used to disperse the spectrum into its component wavelengths either before or after the beam is transmitted through the sample. Nondispersive instruments, by their nature, are limited to monitoring only one pollutant, while dispersive instruments are capable of monitoring several.

Nondispersive infrared spectroscopy has found its greatest use in carbon monoxide monitoring and is the standard reference method for that pollutant. In a typical application, radiation from a broad-band infrared source is passed simultaneously through a reference cell containing either CO-free air or nitrogen and through an atmospheric sample

<table>
<thead>
<tr>
<th>Method</th>
<th>NO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>CO</th>
<th>Hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet chemistry</td>
<td>0.01</td>
<td>0.01</td>
<td>0.002</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>0.005</td>
<td>0.005</td>
<td>0.002</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Electrochemical transducers</td>
<td>0.05</td>
<td>0.05</td>
<td>0.1</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Gas chromatography</td>
<td>10</td>
<td>0.005</td>
<td>0.1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Nondispersive infrared</td>
<td>0.025</td>
<td>0.025</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Dispersive infrared</td>
<td>0.03</td>
<td>0.003</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersive ultraviolet</td>
<td>0.05</td>
<td>0.003</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Minimum concentration to give 1 percent absorption in a 2-meter cell. Minimum concentration to give 1 percent absorption in a 20-meter cell. [Source: James Hodgson, Environmental Protection Agency]
Attenuation of infrared energy is passed first to the radiation produced by $\text{C}^1$0, moisture or other pollutants in the air. If the arc is sufficiently close that the laser beam is then monitored laboratories. S. Navy to monitor CO in nuclear plants. The ratio of transmitted light of the intensities is attenuated equally through a filter that alternately removes the absorption of the infrared. This technique, like that of the Andros instrument, has not been successfully applied to other pollutants, so that its utility appears limited. A further drawback is that such techniques necessitate a separate instrument for each pollutant to be measured, and thus eliminate one of the most significant potential benefits of optical systems.

A partial solution to these problems is embodied in a unique CO monitor produced by Andros, Inc., Berkeley, California. The Andros instrument contains a broadband infrared source that simulates fluorescence of $\text{C}^{16}$O and $\text{C}^{18}$O contained in a sealed cell. The source differential is detected by the phragm and a microphor-like transmitter that converts the differential into an electrical signal suitable for amplification and display. Such an instrument is sufficiently sensitive for most applications and, th other infrared or ultraviolet sources, is readily adaptable to a variety of stable gases. It is, however, highly susceptible to interference by water vapor and strongly absorbing pollutants whose absorption is not canceled by a reference cell. The microphonic detector, furthermore, is extremely susceptible to mechanical vibrations and use severely limits the portability of such instruments.

One solution to some of these problems is embodied in a unique CO monitor produced by Andros, Inc., Berkeley, California. The Andros instrument contains a broadband infrared source that simulates fluorescence of $\text{C}^{16}$O and $\text{C}^{18}$O contained in a sealed cell. The source differential is detected by the phragm and a microphor-like transmitter that converts the differential into an electrical signal suitable for amplification and display. Such an instrument is sufficiently sensitive for most applications and, th other infrared or ultraviolet sources, is readily adaptable to a variety of stable gases. It is, however, highly susceptible to interference by water vapor and strongly absorbing pollutants whose absorption is not canceled by a reference cell. The microphonic detector, furthermore, is extremely susceptible to mechanical vibrations and use severely limits the portability of such instruments.

A partial solution to this problem is exhibited in an ultraviolet ozone detector manufactured by Dasibi Corporation, Glendale, California. In this instrument, the sample gas stream is divided into two portions, and the ozone in one stream is catalytically converted to oxygen. The ozone-free stream then becomes the reference gas, thereby minimizing interference by moisture and other pollutants. But this technique, like that of the Andros instrument, has not been successfully applied to other pollutants, so that its utility appears limited. A further drawback is that such techniques necessitate a separate instrument for each pollutant to be measured, and thus eliminate one of the most significant potential benefits of optical systems.

Microwaves More Promising

An alternative, and potentially more promising, physical method is microwave spectroscopy. Small, polar molecules convert microwave energy to rotational energy at discrete frequencies that are characteristic for each pollutant. Since there is very little overlap in these frequencies, a high degree of specificity can be obtained. The principal drawback to this technique is a lack of sensitivity, since absorption at microwave frequencies is considerably smaller than absorption in the infrared.

Microwave spectrometers are generally operated at low sample pressures (typically about 10^-2 torr) to prevent collisional broadening of absorption bands. At such pressures, however, the absolute number of pollutant molecules is so reduced that detection of ambient concentrations of pollutants may require an unreasonably long microwave cavity or wave guide to provide a sufficiently large sample.

A partial solution to this problem is provided by Laurence W. Hrubesh of Lawrence Livermore Laboratory, who has designed a 15-cm resonating cavity that achieves greater sensitivity by repeatedly passing the microwaves through a small sample. With this wave-guide and state-of-the-art instrumentation, he says, strongly absorbing pollutants such as sulfur dioxide, ammonia, and formaldehyde can be measured accurately in the 100 ppb range. Less polar pollutants, such as $\text{NO}_2$, can be measured at concentrations as small as 10 parts per million.

A further increase in sensitivity can be obtained by preconcentration of the atmospheric sample. One such approach being examined by Hrubesh and Lee Scharpen of Hewlett-Packard Corporation, Palo Alto, California, is the use of gas-permeable membranes. Dimethyl silicone membranes, for example, allow much greater permeation of organic and some inorganic gases than do the major constituents of air. Under appropriate pumping conditions, therefore, such membranes not only provide an approximately hundredfold enrichment in pollutant concentrations, but also produce the required reduced sample pressure. Multipollutant microwave spectrometers embodying such improvements could be on the commercial market in as little as 2 years, Scharpen says. The principal problem that must first be overcome, he adds, is to ensure that the permeation characteristics of the membrane remain constant throughout its lifetime.

A solution to this problem is exhibited in an ultraviolet ozone detector developed by Andros, Inc., Glendale, California. In this instrument, the sample gas stream is divided into two portions, and the ozone in one stream is catalytically converted to oxygen. The ozone-free stream then becomes the reference gas, thereby minimizing interference by moisture and other pollutants. But this technique, like that of the Andros instrument, has not been successfully applied to other pollutants, so that its utility appears limited. A further drawback is that such techniques necessitate a separate instrument for each pollutant to be measured, and thus eliminate one of the most significant potential benefits of optical systems.

A great number of other techniques for monitoring air pollution are also under investigation. One new research development deserves mention; however, it is indicative of the types of instruments that may eventually be used. Earlier this summer, Bernard C. LaRoy and his associates at the Philip Morris Research Center, Richmond, Virginia, revealed a major breakthrough in the development of solid-state electrochemical transducers. They find that thin-film lanthanum fluoride electrolytes are able to transport ions formed by donation of electrons to such reducible gases as $\text{SO}_2$, $\text{NO}_2$, $\text{NO}$, and $\text{CO}_2$.

Miniature electrochemical cells constructed with this solid electrolyte exhibit a conductivity that, above a voltage threshold characteristic of each gas, varies linearly with gas concentration. (The only observed exception, $\text{NO}_2$, exhibits a logarithmic relation between conductivity and concentration.) Few air pollution experiments have been performed with such cells. LaRoy says, primarily because of the novelty of the technique. But, he contends, the properties of the solid electrolyte promise a great increase in reliability, simplicity, and longevity compared to current instruments of all types.

—THOMAS H. MAUGH II
COMPANY: Andros Incorporated 2332 4th Street
ADDRESS: 939-Bright-Way-Berkeley, Calif. 94710
PHONE: (415) 849-1377
KEY ADDRESS:
ASSET RATING:

A-Z PARENTHETICAL: Dual Isotope Fluorescence Analyzers, detectors, recorders, and testers of air for presence of carbon monoxide, air pollution detection devices, auto exhaust & analyzers.

PRODUCT LISTINGS:

Analyzers: Mine & Industrial Air (carbon monoxide, dual-isotope fluorescence)

Analyzers: Exhaust (carbon monoxide, dual-isotope fluorescence)

Analyzers: Trace (carbon monoxide, dual-isotope fluorescence)

Detectors: Gas, Carbon Monoxide, etc.

Gas Analyzers (Carbon monoxide detectors)

X Gas Analyzers: Exhaust (Carbon monoxide detectors)

Air Pollution Control Systems (Carbon monoxide detectors)

Air Pollution Equipment (Carbon monoxide detector)

X Air Pollution Sampling Instruments & Devices (Carbon monoxide detector)

Indicators: Carbon Monoxide

Indicators: Gas (Carbon Monoxide)

Instruments: Air Testing (Carbon monoxide)

Instruments: Measuring (Carbon monoxide detector)

Pollution Control Systems (Carbon monoxide detector)

Recorders: Carbon Monoxide (analyzers, detectors, & recorders)

Recorders: Digital (Carbon monoxide detector)

Recorders: Gas Density (Carbon monoxide detector)

Testers: Air (Carbon monoxide)

Testers: Automobile (Exhaust analysis, CO)
Testors: Combustion (Carbon monoxide detection)
Testors: Gas, Sulphur, etc. (carbon monoxide detector)
Testing Equipment (Automobile Exhaust)
NOTES ON ANALYTICAL INSTRUMENTATION

THE FLUORESCENT CO ANALYZER

A new approach to the use of infrared absorption gives this instrument improved selectivity and performance in CO monitoring.

by F. W. Karasek

Department of Chemistry, University of Waterloo, Waterloo, Ontario
The toxicity and wide occurrence of carbon monoxide make its accurate measurement and monitoring in trace concentrations important. This gas is a product of most combustion reactions, and as a result represents one of the most widespread pollutants. Concentrations as high as 30 - 50 ppm generated by dense automobile traffic are found in some urban areas. Carbon monoxide affects humans by reducing the ability of the bloodstream to carry oxygen to body tissue by displacing oxygen from hemoglobin to form carboxyhemoglobin. A person continuously exposed to air containing 10 ppm carbon monoxide will reach carboxyhemoglobin levels greater than 2%, at which point effects upon the nervous system become apparent (1).

Carbon monoxide monitors must reliably measure concentrations in the 10 ppm and lower range. Applications for these instruments are numerous and include continuous monitoring of urban areas and of industrial sites such as tunnels, garages, factories and mining facilities. In addition, there is an increasing number of medical uses, particularly those associated with breath analysis concerned with the study of diseases and the monitoring of the condition of patients.
The present instruments used for these applications are generally those based on the non-dispersive infrared absorption of carbon monoxide (2). Detectors used most often are the selective (but vibration-sensitive) gas-filled capacitance-microphone type. As well designed and reliable as these instruments are, there are still improvements in sensitivity, selectivity and reliability needed that would broaden their scope and usefulness.

A recent instrument based on the electrochemical oxidation of carbon monoxide is one approach in these directions (3). Although quite sensitive and portable, with a very fast response time, this instrument is not too selective against certain interfering components. Its discrimination against such gases as \( \text{H}_2\text{S} \) is 40 to 1; against \( \text{C}_2\text{H}_4 \), only 4 to 1.

**IR Fluorescence Provides Selectivity**

The most unusual approach to enhancement of all three factors of selectivity, sensitivity and stability is found in the Andros 7000 infrared CO-analyzer (4). Its unique capabilities arise because the energizing radiation passing through the sample consists of two very narrow, selective infrared bands, one exactly matching the vibrational-rotational absorption bands of CO for sensing CO concentration, the other serving as a reference. These bands are created by the fluorescence
generated in a cell filled with equal amounts of CO\textsuperscript{16} and CO\textsuperscript{18} when the cell is irradiated by a broad band IR source. By use of a rotating filter, alternate pulses of these emitted bands are passed through a single sample cell. Since naturally occurring CO contains 99.8 percent of the CO\textsuperscript{16} isotope, the CO\textsuperscript{16} band will respond absorbed by the CO concentration in the sample cell, while the CO\textsuperscript{18} band will be unaffected and can serve as a reference. With a single optical path and sample cell, use of a ratio comparison of these two signals results in a measurement relatively free of drift and sensitivity changes. Transmission of the optics can change by 50 percent without degrading performance. This provides a large tolerance to condensation of particulates in the sample and source or detector drift.

The optical system shown in Fig. 1 reveals the essential components of the instrument. The rotating (5000 rpm) chopper and filter wheels provide the alternate radiation pulses which are synchronously detected by the electronics to give the ratio output signal. The lead selenide detector is a solid-state/photodiode thermally stabilized at -30°C for maximum sensitivity by a Peltier cooler. The performance characteristics include a noise
level of 0.05 ppm, rejection ratio of the common H₂O and CO₂ interferences of at least 4000 to 1 and a 25-second response time.

ANDROS BEGINS ITS PRODUCTS WITH IR

Arkon Scientific Laboratories was organized about 4 years ago to perform government contract work for NASA and the EPA. From work done to develop a flight CO-monitor for the NASA Skylab project the technology to design the fluorescent IR analyzer was evolved. When Andros, Inc. was formed recently from the former Arkon organization this instrument became its first product.

The design of the instrument (Figs. 2 and 3) bears many signs of the aerospace skill of its originators: it is compact and lightweight with easily serviced solid-state electronics.

The new ANDROS company of nearly 50 people plans to continue contract research work of the type that will lead to viable new instrumentation products (5). Current interests lie in the pollution and medical areas. Approaches similar to that of the fluorescent CO-analyzer are being taken to monitor traces of other gases such as NO and CO₂. An electro-mechanical drive for a fully implantable artificial heart is under study. In another project at the U.C. Medical Center in San Francisco, the CO-analyzer is being evaluated to test human lung
These tests involve measuring the CO response curve during exhalation of a single breath that initially contained 3000 ppm of CO.

The pollution and medical areas are broad ones for creation of new instrumentation. Although the IR analyzer is one of the oldest and best developed instruments, it is encouraging to see that new approaches like the Andros instrument are still appearing.
REFERENCES


CAPTIONS

Figure 1. Schematic of the ANDROS 7000 CO-analyzer.
The components shown are: A - synchronous motor, B - IR source, C - chopper disk, D - windows, E - dual isotope fluorescent cell, F - CO16 filter, G - isotope filter disk, H - CO18 filter, I - window, J - magnet pick-up of synchronous pulses.

Figure 2. The CO-analyzer unit shows push-button range switches and trouble-indicating lights along with a meter scale linear in CO concentration.

Figure 3. An exposed view of the instrument reveals the compact optical system and plug-in electronics. The light-emitting diodes on the boards are used to indicate malfunctions for troubleshooting.
SPECIFICATIONS

Range:
20, 50, 100, 200 ppm.

Sensitivity:
0.02 ppm.

Accuracy:
1% of reading +1% of full scale.

Specificity:
Inert interferent rejection:
H2O: 10,000:1
CO2: 20,000:1
The rejection ratio to all other common interferents is at least 10,000:1. Consult factory for details.

Opacity Tolerance:
No degradation of performance when measuring in a medium of up to 50% opacity.

Noise:
0.2 ppm RMS.

Span Drift:
(at constant temp)
1% of full reading/month.

Zero Drift:
(at constant temp)
1% of full scale/week.

Span Temp. Coef:
0.01% of reading/°F change in ambient temperature.

Zero Temp. Coef:
0.01% of reading/°F change in ambient temperature.

Response Time:
25 seconds to 90% of full reading (Option 04-1).

Output:
5 volts.

Warm-up Time:
20 minutes to full accuracy.

Ambient Temp:
+32° to +122°F.

Ambient Relative Humidity:
50%

Power:
115/230 VAC; 50-60 Hz; 125 watts.

Size:
6 1/2" x 10 1/2" x 6 3/4".

Weight:
32 lbs.

Mounting:
Standard Reims Flack.

Options:
Option 01: Internal Sample Pump
Option 02: Internal Zero Calibrator
Option 03: Digital Readout and BCD Output
Option 04: Fast Response

Price:
$650.

ANDROS
ANDROS (formerly Arkon Scientific Laboratories) has developed the Dual-Isotope Fluorescence CO-
 analyzer over 2½ years of R&D contracts with NASA and EPA. D.I.F. CO-analyzers have been delivered
by ANDROS to NASA for use on board "Skylab" orbiting laboratory and to the U.S. Navy for use
in nuclear submarines.
At the ANDROS facilities in the San Francisco Bay Area (near the UC campus at Berkeley), our staff
of scientists are developing a broad line of advanced scientific instruments, devices and systems for en-
vironmental, medical and industrial applications. ANDROS is dedicated to building "Instruments for Life"," and pursuing new technologies to attain sig-
ificant achievements in measurement capability.

ANDROS Instruments For Life
930 Dwight Way, Berkeley, Calif. 94704
Phone: 415-845-1377

Andros 7000 Carbon Monoxide Analyzer
With Dual-Isotope Fluorescence

- Rejects Interference By Water-Vapor and Non-
  CO Gases.
- Maintains Measurement Stability and Repea-
  tibility at CO Trace Concentrations Below 1 ppm.
- Immune To Shock and Vibration Through Utili-
  zation of Non-Microphonic Solid-State Detectors.
The ANDROS 7000 Produces Stable and Accurate
Trace CO Measurements Even When Operating
In Vehicles, Boats or Aircraft.
- Free of Drift or Errors Caused By Condensation
  or Particulate Accumulation On Optics.
- Sustains Calibration For At Least 30-Days. Even
  In Field Operation.
- Yields Fast Response Measurements.
- Meets EPA Accuracy and Reliability Require-
  ments.

Postage Will Be Paid By:
ANDROS, INC.
930 Dwight Way
Berkeley, California 94704

First Class Postage Permit No. 109S
San Francisco, Calif.
New Andros CO Analyzer Offers FPM Accuracy Even In Vans, Trailers And Aircraft

Andros, Inc. (formerly Arkan Scientific Labs) has just announced the ANDROS 7000, a unique atmospheric carbon monoxide analyzer combining unmatched sensitivity (0.2ppm) and high specificity (immunity to water vapor, or non-CO gases) in a rugged, compact package. Unlike conventional CO monitors, the ANDROS 7000 will perform reliably in monitoring vans, boats and even helicopters.

**Sensitivity**

The ANDROS 7000 permits measurement of trace concentrations of carbon monoxide below 1ppm, with better than 0.2ppm accuracy. Due to the high degree of stability inherent with the D.I.F. (Dual-Isotope-Fluorescence) technique, the ANDROS 7000 produces believable and repeatable measurements at these low levels, without the need for frequent zero and span checks.

**Specificity**

The ANDROS 7000 is inherently immune to interference from water vapor or other gases present in the sample under test, eliminating the need for troublesome gas conditioning systems. The high specificity to carbon monoxide exhibited by the 7000 is attributable to the use of spectrally specific IR energy, which is generated by carbon monoxide fluorescence. This specific IR radiation can be absorbed only by carbon monoxide present in the gas sample.

The ANDROS 7000 CO analyzer operates at pressures sensitive to shock and vibration.

**ANDROS 7000**

In the ANDROS 7000, an entirely new approach is used to eliminate the performance and reliability problems inherent in traditional D.I.F. CO analyzers. This is accomplished by ANDROS' Dual-Isotope-Fluorescence D.I.F. technique, in which the 7000 alternately produces two IR radiation spectra that are a match of the vibrational-rotational absorption bands of CO₁₆ and CO₁₈. These two IR radiation spectra 'time share' the single sample chamber, producing a sequence of CO concentration and reference signals which are sensed by a solid-state detector.

The ANDROS 7000 detector is a solid-state IR photo-diode which is mechanically rugged and non-microphonic. The detector is operated at peak CO-sensitivity through thermal stabilization at -30°C by a Peltier cooler.

**TECHNICAL DATA**

(please indicate your interests to receive selected mailings of ANDROS technical data.)

- Environmental Monitoring
- Medical & Clinical Applications
- Laboratory Research
- Industrial Process Monitoring & Control
- New Gas Analyzers
- Detailed Technical Brochure on the Andros 7000
- Please maintain my name on your mailing list to receive further Andros literature.

**APPLICATION INFORMATION**

(If you have an immediate potential application for the ANDROS 7000, please include data on expected concentration range, temperature, desired data output format and other significant details of your application.)

**PRICE/DELIVERY QUOTATION**

Please have an ANDROS representative contact me to provide a quotation on your Model 7000. My telephone number is: 415-849-1377

930 Dwight Way, Berkeley, Cal. 94704
APPENDIX B

LETTER FROM R. DONOVAN, RTI, TO
TODD ANUSKIEWICZ, GWU, 20 NOVEMBER 1972,

WITH TWO ENCLOSURES:

- List of Arkon contracts leading to development of CO monitor.

Mr. Todd Anuskiewicz
Biological Sciences Communication Project
The Medical Center
The George Washington University
2001 S. Street, N.W.
Washington, D. C. 20009

Dear Todd:

In response to your recent telephone inquiry as to the patent history of the Andros 7000, I have some information to pass on from Don Willett of Andros. He tells me that only one patent has been filed, although it includes some 27 claims. They expect it to be issued in three or four months. It has serial number 859326, filed September 19, 1969 with the title, "A Fluorescent Source Nondispersive Infrared Gas Analyzer," author, Bill Link, assigned to Arkon Scientific Laboratories. The patent includes the application of isotopes of CO as the fluorescent source (as the Andros 7000 incorporates) plus the use of the isotopes of other gases with those of CO plus the use of the isotopes of other gases alone. They tell me now that the only combination that has proven practical has been the use of the CO isotopes alone. In fact, one of the EPA contracts (that for the nitrogen oxide fluorescent source detector) was a program to develop a fluorescent source using various NO isotopes. This has not worked out well.

I am also enclosing a summary of their gas analysis contracts. From a monetary standpoint it is clear that the bulk of this support has come from NASA. In fact the only CO project supported by anyone else was the NAPCA (EPA) contract that began on June 1, 1970. This was a good seven months after NASA initiated their feasibility study for this general development. The NAPCA program did result in a prototype which had some shortcomings,
none of which were corrected by NAPCA. EPA essentially signed off after that initial experience and has let NASA carry the development so far as CO goes.

I am also enclosing a reprint of the paper from the R&D magazine which is substantially what you received previously.

Sincerely yours,

Bob

R. P. Donovan

cc: Don Willett/Andros
    Charles Eastwood/NASA Hdqts.
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Grand Total $1,272,039.00

A = National Aeronautics and Space Administration
CA = National Air Pollution Control Association
O = Air Pollution Control Office
E = Environmental Protection Agency
M = Bureau of Mines
Assistant Secretary of Labor
George C. Guenther tells how the Occupational Safety and Health Act will affect you and I.

Also in this issue:
Computer languages and programs
NOTES ON ANALYTICAL INSTRUMENTATION

Infrared fluorescence analysis

Recently developed technique uses instrument that compares spectral line absorption of two oxygen isotopes to determine CO concentrations. Similar approaches are being studied to monitor other gases and to test human lung diffusion capacity.

by F. W. Karasek
Department of Chemistry, University of Waterloo, Waterloo, Ontario

The toxicity and wide occurrence of carbon monoxide make its accurate measurement and monitoring in trace concentrations important. This gas is a product of most combustion reactions, and as a result represents one of the most widespread pollutants. Concentrations as high as 30 to 50 ppm generated by dense automobile traffic are found in some urban areas. Carbon monoxide affects humans by reducing the ability of the bloodstream to carry oxygen to body tissue by displacing oxygen from hemoglobin to form carboxyhemoglobin. A person continuously exposed to air containing 10 ppm carbon monoxide will reach carboxyhemoglobin levels greater than 2 per cent, at which point effects upon the nervous system become apparent.

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Although quite sensitive and portable, with a very fast response time, this instrument is not too selective against certain interfering components. Its discrimination against such gases as H2S is 40 to 1; against C2H2, only 4 to 1. One might also expect some degree of zero and span drift.

The most unusual approach to enhancement of all three factors of selectivity, sensitivity, and stability is found in the Andros 7000 infrared CO-analyzer. Its unique capabilities arise because the energizing radiation passing through the sample consists of two bands of very narrow, selective infrared spectral lines, one exactly matching the vibrational-rotational absorption lines of CO for sensing CO concentration, the other serving as a reference. In considering specificity, the distinction between spectral lines compared to broader "bands" is important. These spectral lines are created by the fluorescence generated in a cell filled with equal amounts of CO16 and CO18 when the cell is irradiated by a broad band infrared source. By use of a rotating filter, alternate pulses of these emitted spectral lines are passed through a single sample cell. Since naturally occurring CO contains 99.8 per cent of the CO16 isotope, the CO16 lines will be absorbed by the CO concentration in the sample cell, while the CO18 lines will be unaffected and can serve as a reference. With a single optical path and sample cell, use of a ratio comparison of these two signals results in a measurement relatively free of drift and sensitivity changes. Transmission of the optics can change by 50 per cent without degrading performance. This provides a large tolerance to condensation of particulates in the sample and source or detector drift.

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The pollution and medical areas are broad ones for creation of new instrumentation. Although the infrared analyzer is one of the oldest and best developed instruments, it is encouraging to see that new approaches like the Andros unit are still appearing.

References
APPENDIX C

LETTER FROM CONRAD S. JOSIAS, PRESIDENT,
ANALOG TECHNOLOGY CORPORATION
TO R. P. DONOVAN, RTI, 30 OCTOBER 1972.
SUBJECT: DEVELOPMENT OF A MASS SPECTROMETER.
30 October 1972

Dr. R. P. Donovan  
Research Triangle Institute  
P.O. Box 12194  
Research Triangle Park, N.C. 27709

Dear Dr. Donovan:

A copy of your letter of June 5, 1972 to our Dr. Wilson Brubaker recently crossed my desk for a second time. As a result of my renewed interest in your comments, I decided to send you this letter as an expression of our continuing desire and ability to contribute to the technologies you have discussed.

On 29 September 1970, I sent a letter to Dr. Elliott Harris of NASA MSC telling him of our interest in participating in a program for the measurement of trace constituents in the Skylab cabin atmosphere (copies of our correspondence are attached). Since our Company had, just prior to that time, submitted a proposal to the Naval Ship Engineering Center (NAVSEC) for a comparable system to monitor submarine atmospheres, I included a copy of that proposal to Dr. Harris. Our letter to Dr. Harris spoke about our submitting an unsolicited proposal along the lines of the computerized mass spectrometer approach we had suggested to the Navy. At that time, our ability to proceed with such a proposal effort depended on knowledge of such factors as whether there was a basic similarity between the submarine and Skylab environments. We also believed then that the proposed analyzer would be of particular interest to NASA inasmuch as it uses a mass spectrometer patterned after an instrument developed by ATC under contract to NASA - namely, the tandem quadrupole.

We subsequently received a note from the MSC Small Business Office about correct procedure for submitting unsolicited proposals to MSC but heard nothing further from Dr. Harris.

Our interest in the Skylab program was renewed by your letter of June 5th, which excited some new speculation about the use of the tandem quadrupole approach. Please
be assured that we are as interested today as we were then in becoming familiar with Dr. Harris' requirements and contributing to the Skylab program. The proposal that you mentioned his wanting to see is probably the one for the submarine application, and that is the document I sent to him on September 29, 1970.

Because ATC has now past many noteworthy milestones in its NASA-funded mass-spectrometer technology since our first inquiry to Dr. Harris, I am taking the liberty of enclosing the following three pertinent documents for your general information.

1. The technical portion of ATC's proposal to NAVSEC for a Submarine Atmosphere Analyzer;

2. A copy of a proposal to NASA Marshall Space Flight Center for a Residual Gas Analyzer (RGA); and

3. A brochure describing ATC's Respiratory Gas Analyzer.

The proposal to the Navy was based on the use of the tandem quadrupole that ATC was subsequently to develop on a NASA contract. The RGA was for a contamination monitor, which also used the tandem quadrupole. In that proposal, the mass spectrometer description reflected the large amount of work that had transpired in the interval between the Navy and NASA proposals. The respiratory gas analyzer is essentially the laboratory version of the astronaut instrument developed for NASA MSC. This instrument is scheduled to be delivered shortly to our customer at MSC.

Although ATC's proposal to NAVSEC is based on the analysis of components by measurements of individual parent or dominant peaks, there is another analysis approach worthy of mention here, which has been reported on internally at ATC. This alternative technique, which we call spectrum stripping, is based on the preprogrammed, computerized subtraction from a basic cracking pattern of all other components known or guessed to exist in the atmospheric sample with mass peaks superimposed on those of primary interest. The nominal cracking pattern, when stripped of interfering contributions, is then automatically corrected by a least squares fit to the remaining data. This technique becomes attractive as a tool for preserving accuracy when normally straightforward measurements of parent or dominant peaks become partially masked.
by superimposed background components.

We would very much appreciate any recommendations you might offer to Dr. Harris and others at MSC about our special instrumentation capabilities and sustained interest in this area of Skylab atmosphere analysis. We will be happy to follow up with a personal call to Dr. Harris, if required.

With respect to the contacts that you referred to at the National Institute for Occupational Safety and Health (NIOSH), Dr. Brubaker spoke to Dr. Charles Xintaras of NIOSH on May 12, 1972 and learned of Dr. Xintaras' work in correlating the deteriorated neural responses of industrial workers and their environments. He, too, visualized a van-mounted equipment to be taken to various plants to monitor metabolized derivatives in the blood and alveolar breath gas of the workers.

While Dr. Xintaras expressed the need for better instrumentation for analyzing inhaled and exhaled breath gas, at the time of that conversation, his funds for the coming fiscal year (FY '73) had already been committed. He did recommend, however, that we contact Dr. Marcus Key of NIOSH to discuss these and related matters further—something we plan to do in the near future.

In regard to your question as to the feasibility of a vehicle-mounted air pollution monitor using a mass spectrometer, our opinion is that the requirements associated with such a monitor are sufficiently similar to those of the instrument we have proposed to the Navy that we believe our approach to be quite practical for the vehicle-mounted application.

Consider, for example, the mass-filter approach used in the Astronaut breath analyzer as a representative configuration for this application. We are particularly proud of the resolution and peak shape achieved with the miniature quadrupole used in this device especially as it might apply to trace-gas analysis. For a peak width of about 0.42 amu, this 2-inch quadrupole provides symmetrical 10⁻¹ valleys at unit mass separation (i.e. the amount of residual skirt amplitude of an interfering peak at the center of an adjacent mass peak is down to 10⁻¹ of the value at the center of the interfering peak.) Usable to a range of better than 200 amu, this basic design, if modified with a tandem curved
section and/or an off-axis multiplier, will provide the performance necessary for a vehicle-mounted pollution monitor as specified in the attachments to your letter. ATC is definitely interested in building such an analyzer, and its design would indeed be strongly influenced by highly pertinent work accomplished on NASA-funded contracts, which are as follows: NAS9-11307 (MSC), NAS9-12765 (MSC), 952835 (JPL), and NAS9-8371 (MSC). Further details on the astronaut breath analyzer and lunar quadrupole may be obtained from Dr. John Rummel of NASA MSC and Mr. Floyd Roberson of NASA Hq., respectively.

If this opportunity is still active, we would like to have your opinion as to the most efficient method to initiate our participation. For example, if you are in this part of the country, we would welcome your visiting us so that we might discuss an approach to the monitoring configuration. If that is not practical, we would be happy to have one of our representatives call on you at Research Triangle Park.

I look forward to your comments and welcome any suggestions you might offer along the lines just discussed.

Very sincerely,

ANALOG TECHNOLOGY CORPORATION

Conrad S. Josias
President

CSJ:nb
Attachments

cc: Dr. John Rummel, NASA, MSC
    Mr. Floyd Roberson, NASA Hq.
APPENDIX D

November 3, 1972

Mr. R. B. Donovan  
Research Triangle Institute  
P. O. Box 12194  
Research Triangle Park, N. C. 27709

Dear Mr. Donovan:

Thank you for your call concerning the reports on our contract with NASA/EPA. I am sorry for having neglected to include you on the distribution. Hereafter, you will receive all reports. Enclosed is a copy of the first quarterly report on the project. Please feel free to call for any additional information.

Sincerely,

L. W. Hrubesh  
General Chemistry Division L-404

LWH:gw
FEASIBILITY STUDY OF A GUNN DIODE MICROWAVE CAVITY SPECTROMETER AS A FORMALDEHYDE GAS MONITOR

QUARTERLY REPORT
June - August 1972

Contract No. EPA-IAG-D179(D)
NASA-L-75902

September 19, 1972

Prepared by
L. W. Hrubesh
University of California
Lawrence Livermore Laboratory

Project Officers
Dr. James Hodgeson
Environmental Protection Agency
Research Triangle Park, N.C. 27711

Mr. William White
National Aeronautics and Space Administration
Hampton, Virginia 23365
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I. Status Report
   A. Establish Theoretical Limit of Detectability

   The 3+3 pure rotational transition of the formaldehyde molecule at 28,974.80 MHz was selected for monitoring purposes. This absorption line is quite strong (coefficient \( \approx 1.6 \times 10^{-4} \) cm\(^{-1}\)), has no known interferences from other gases, and is in a frequency range where the solid state sources are available and are not prohibitively expensive.

   The maximum possible quality factor \( Q_L \) for the cavity resonator absorption cell is desirable for optimum sensitivity. The operating \( Q_L \) is maximized by careful construction of the resonator (alignment and mirror finishes), by choosing the proper resonant mode, and by reducing the loading of the resonator by external detectors. We have constructed various models and have made appropriate measurements for determining optimum cavity \( Q_L \). We determine this value to be \( Q_L \approx 20,000 \) for our absorption cell.

   The theoretical sensitivity limit for the \( H_2CO \) 3+3 rotational line in a resonant structure whose \( Q_L = 20,000 \) can be calculated from the following equation:

   \[
   \gamma_{\text{min}} = \frac{h k T \Delta f}{P_{\text{in}}} \cdot \frac{2 T}{Q_L \lambda}
   \]

   where

   \( \gamma_{\text{min}} \) = the minimum detectable absorption coefficient of the system
   \( k \) = Boltzmann's constant
   \( T \) = absolute temperature
   \( N \) = noise figure for the system
   \( \Delta f \) = detection bandwidth
   \( P_{\text{in}} \) = microwave power delivered to the cavity
   \( \lambda \) = the wavelength of radiation
We expect to operate with a detection bandwidth ($\Delta f$) of 0.1 Hz and a microwave input power of approximately 5 milliwatts. We have not as yet measured $N$ for the system but expect it to be less than 100. With these values and room temperature

$$\gamma_{\text{min}} \approx 1.73 \times 10^{-12} \text{ cm}^{-1}$$

Since $\gamma \approx 1.6 \times 10^{-4} \text{ cm}^{-1}$ for the $\text{H}_2\text{CO} 3\rightarrow 3$ line, we calculate a theoretical detectability limit of:

$$\gamma_{\text{min}}/\gamma \approx 11 \times 10^{-9} \text{ or 11 ppb.}$$

B. Determine Techniques, Conditions and Parameters for System Design

Some of the major concerns about using a resonant cell in a microwave spectrometer system are: its sensitivity to microphonics and gross mechanical vibrations or shocks, its thermal instabilities, and shifts in resonant frequency due to changes in the total permittivity of gases within it. For completely automatic operation of the spectrometer, all of the above effects are compensated by a servo control, and nearly absolute frequency stability is obtained. This can be accomplished by comparing the resonant frequency of the cavity cell with that derived from an extremely stable crystal controlled oscillator; an error signal can be derived from any difference and used to control the cavity frequency in a feedback loop. Thus, the cavity resonant frequency can take on the stability of the crystal controlled oscillator (stability $\pm 1$ part in $10^7$ per day). We have accomplished this kind of stability for our system with the elements shown in Fig. 1. Item A is a $2,900.3853 \pm 0.0001$ MHz crystal stabilized oscillator. Its output is passed through an RF sampler (Item B) to a crystal harmonic mixer and detector diode (Item C). Here the 10th harmonic of oscillator A is mixed with the microwave frequency from Gunn diode (Item D). When their difference is 30 MHz, this signal is passed through Item B onto IF amplifier (Item E) and its phase is compared with that of a stable
oscillator (Item F). Any difference in phase is amplified (Item G) as an error signal and is used to drive the speaker coil (Item H) which changes the dimensions of the cavity and thus its resonant frequency.

Sensitive detection of absorption produced by formaldehyde within the cavity will be obtained by using the same electronics involved in the servo control. A dc voltage is applied between the two plates which make up the resonator (Item I) and it is switched on and off in a square wave fashion at a rate of 1 kHz. When the field produced by this voltage is on, it effectively moves the peak of absorption to another frequency; when it is off, the peak absorption occurs at the monitored frequency. Thus, the microwave energy passing through the cavity onto the detector (Item C) is slightly amplitude modulated by the gas absorption at a rate of 1 kHz. The 30 MHz intermediate beat frequency leaving the mixer detector then also carries the amplitude modulated information. After the 30 MHz signal is amplified in the IF amplifier (Item E) it is detected a second time to demodulate the carrier and leave just the 1 kHz signal. The 1 kHz signal is then phase compared with a reference 1 kHz signal in the lock-in detector (Item J), the output of which is the signal corresponding to the molecular absorption. This signal is available for both meter readout and recording.

The design for optimizing the coupling of the Gunn oscillator and the detector to the cavity has been finalized. Considerations for a simple electronic calibration of the system are presently being made.

C. Construction of a Breadboard Model

A breadboard model has been constructed which embodies the electronic design indicated in B. We have observed the expected frequency stability of approximately one part in $10^7$ per day. The electronic design includes an automatic search and lock mode to facilitate a single on-off switch operation and to insure a "locked" condition after a gross mechanical shock.

We are preparing a preliminary test of the detection system, but as yet we have not had any gas in the breadboard model.
oscillator (Item F). Any difference in phase is amplified (Item G) as an error signal and is used to drive the speaker coil (Item H) which changes the dimensions of the cavity and thus its resonant frequency.

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We are preparing a preliminary test of the detection system, but as yet we have not had any gas in the breadboard model.
Figure 1 - Block Diagram of Electronic System Design

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Crystal Stabilized S-Band Oscillator</td>
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<tr>
<td>B</td>
<td>RF Sampler</td>
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<tr>
<td>C</td>
<td>Harmonic Mixer-Detector Diode</td>
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<td>D</td>
<td>Gunn Effect Diode</td>
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<td>E</td>
<td>IF Amplifier</td>
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<td>F</td>
<td>Crystal Stabilized 30 MHz Oscillator</td>
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<td>DC Amplifier</td>
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<td>Speaker Coil</td>
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<td>I</td>
<td>Resonant Cavity</td>
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<td>K</td>
<td>Recorder</td>
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<td>L</td>
<td>Stark Modulator</td>
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<tr>
<td>M</td>
<td>Phase Detector</td>
</tr>
<tr>
<td>N</td>
<td>Gunn Diode Power Supply</td>
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E. Examination of Sample Handling and Concentrating Techniques

A cursory evaluation of various concentration techniques for use with formaldehyde vapor and the microwave spectrometer has been made. A silicone membrane separator appears to be the best choice both because of its successful use in mass spectrometric systems, and it's the promise from some preliminary work done here on an earlier prototype.

We have constructed a two-stage separator device for use with silicone rubber membranes. The design is similar to one used effectively at LLL for a gas chromatograph-mass spectrometer interface for various organic compounds. We are making some preliminary tests with this device by using the chromotropic acid colometric test for formaldehyde and formaldehyde permeation tubes prepared for us by Dynascience, Inc. This will offer an independent check against our results with the microwave spectrometer detector. We are, however, having problems with the rubber membrane material for the separator (see a following section).

Because of its high relative concentration in ambient air, it will be desirable to remove most of the water vapor from the flow of ambient air into our separator. We have purchased a membrane device from Perma Pure Products, Inc., which is expected to dry ambient air by a factor of as much as 500:1. Our preliminary tests with this device indicate that it indeed can dry a wet air sample and that its ability to dry is a strong function of the flow rate through it. This device promises to offer the reduction in water vapor required for our spectrometer system.

F. Critical Measurements on the Formaldehyde 3→3 Spectral Line

Critical data will be required for the absorption line chosen for monitoring purposes. We have contracted Professor E. A. Rinehart and the University of Wyoming to make the measurements since the required equipment is already available there. The following information will be derived from the critical data supplied by Professor Rinehart.
1. A determination of the Stark voltage just necessary for maximum response from the $H_2CO$ $3\rightarrow 3$ line for total pressures up to the maximum obtainable in a waveguide Stark cell.

2. A determination of how the microwave power necessary to obtain peak signal changes with partial pressure of $H_2CO$ in $N_2$.

3. A determination of how the signal changes versus total pressure at constant input power.

4. The determination of the linewidth parameter for both pure $H_2CO$ and $H_2CO$ in mixtures with dry $N_2$ gas.

II. Problem Areas

A. Frequency Stabilization

The method that we are presently using to physically change the resonant frequency of the cavity for frequency stabilization has several drawbacks. One, it requires locating a speaker coil directly within the vacuum chamber; two, the resulting support for the movable plate is not mechanically stable and is extremely sensitive to vibration; three, the movable plate is required to be very light and has sharp edges, a potential source for electrical breakdown. We are presently testing other methods of tuning the resonant cavity which would not require drivers inside the sample chamber.

B. System Noise

We are experiencing much system noise which we can correlate to the mechanical vibrations that the cavity picks up from the laboratory environment. The frequency stabilization loop, of course, compensates for this type of noise; however, this noise can cause problems in the detection electronics. When we test the detection system with formaldehyde we can evaluate the effect of this noise. We hope to be able to design a much more mechanically stable cavity, while still tunable, thus reducing the source of the noise.
C. Modulation

We anticipate problems with the Stark modulation technique on the resonant cavity. Prior work in this area with the prototype model revealed premature breakdown and ionization problems because of the geometry of the cavity. We are trying to determine the cause for this effect and are taking precautions in our cavity design wherever possible.

D. Faulty Membranes for Separator

We have been purchasing silicone rubber membrane material from a single commercial source. We are finding this material to be inconsistent from batch to batch and have found a large number of pin holes in most batches. An effort is being made to locate another source for the membrane material. Some consideration is being given to making our own if the material continues to be unreliable.
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<td>C. Maninger</td>
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<td>J. Frazer/K. Ernst</td>
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<td>Environmental Protection Agency</td>
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<td>Research Triangle Park, N.C. 27711</td>
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<td>Mr. William White</td>
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<tr>
<td>National Aeronautics and Space Administration</td>
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<td>Langley Research Center</td>
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<td>Hampton, Virginia 23365</td>
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APPENDIX E

LETTER FROM FRANKLIN A. AYER, RTI, TO
TODD ANUSKIEWICZ, GWU, 1 NOVEMBER 1972 WITH ENCLOSURE ENTITLED,
"TECHNOLOGY TRANSFER POTENTIAL OF THE BLUE CRAB MONITOR."
November 1, 1972

Mr. Todd Anuskiewicz
Biological Sciences Communication Project
George Washington University
2001 S. Street
Washington, D.C. 20009

Dear Todd:

Reference is made to your letter of 4 October. The attached paper based on Bob and my visit to the Atlantic Estuarine Fisheries Center should answer most of your questions about the blue crab experiment.

I came away from the meeting terribly enthusiastic about Dr. Engel's work and I believe that if NASA will consent to take the program one step further that a marketable instrument will result.

The objective of Dr. Engel's research is to understand the mechanism of the regulation of the internal environment of the crab in relation to the external environment. This involves, basically one factor—the ionic component of the blood of the crab which is characterized by conductivity. The same experiment could be run for lobsters.

The objective of the research to be performed with the new temperature-compensated instrument would remain the same but the temperature/salinity interchange would be better understood. In fact this would be the beginning of understanding the environmental aspects and its effects on the animal. As you can see this would have a tremendous impact on the crabbing industry.

Field tests are not planned as the work performed in the model estuary is roughly equivalent to a field test and can be better controlled—particularly the antenna which needs an occasional adjustment. (This is a minor problem at the moment.)

The Estuary Center is a basic research laboratory. In working with the AEC they tend towards projects that are more practical in application. However, I believe that this project eventually will have a practical application of a rather great magnitude. One of the steps towards practicality is the need to better understand the characteristics and physiological aspects of the animal so that crab and fish kills can be prevented. This is where salinity/temperature enters into the picture. There may be a combination of salinity/temperature, zinc concentration, etc., which may be very lethal. Understanding this could be used to determine if maximum concentrations by law of cadmium, zinc, radiation, carbon monoxide, etc. are realistic. If all the allowed concentrations of pollutants occur at one time could they cause crab and fish kills? This is not known today.
Research schedules with the new instrument is dependent on the availability of the instrument and Dr. Engel's work load. With a full time technician (which Dr. Rice, Center Director, has stated be would give him) Dr. Engel believes a significant amount of work could be done in a year. This is discussed above and in the attached paper. Also other applications are discussed in the paper. Undoubtedly another experimentation step is needed before the instrument will have a good deal of commercial appeal. As you know there is no known instrument that will do what is being proposed.

I hope the attached paper will help "sell" this program as I feel it is very worthwhile.

Sincerely,

Franklin A. Ayer

FAA/meg

Enclosure
"Technology Transfer Potential of the Blue Crab Monitor"

As documented in a case study entitled, "A New Technique for Measuring the Osmo-Regulation of Blue Crabs," (Marine Science Application, RTI/OC-16), microelectronics specialists at the Langley Research Center have developed a conductivity probe and transmitter/receiver apparatus which is capable of monitoring continuously the conductivity of the blood of a blue crab while the crab is immersed in a salt water bath at 20°C. The key benefit of this experiment has been the generation of data measuring the response of many blue crabs to salinity shock. These data have provided valuable information about the adaptability of the blue crab to changes in the salt content of its surroundings.

All the work to date, however, has been carried out at 20°C in a well controlled temperature bath. A valuable next step now is to incorporate the effect of temperature into the study. Unfortunately, the present transmitter does not operate at temperatures greatly different from 20°C. The principal investigator from the Atlantic Estuarine Fisheries Center, Dr. D.W. Engel, has recently requested a temperature compensated transmitter for including the effects of temperature in his experiments. Honoring that request will require additional NASA TU support and therefore, demands a reappraisal of the technology transfer potential of the NASA monitoring system. Such a reappraisal is the purpose of this report.

The existing monitoring system makes continuous measurements on living animals, the only instrument known to RTI and the Atlantic Estuarine Fisheries Center with such a capability in invertebrates. Conventional techniques are to take periodic samples of an animal's blood, breath, etc. or to section an animal in order to determine ion distribution for example. Another common experimental method is the generation of LD50 plots—the determination of the exposure needed to kill 50% of the test animals. The NASA built system can detect the onset of adverse effects far below the lethal threshold, which makes it very versatile and valuable.
As such the system is of high interest for studies in other species. How readily the instrument could be adapted for use on other species is not clear. Marine biologists, upon viewing (or learning of) the experiment, come away quite interested and impressed but generally balk at the presumed high price tag so that the NASA technique has not yet spread beyond the Atlantic Estuarine Fisheries.

On the other hand, publicity to the marine science technical community has been relatively limited. Dr. Engel has made three oral presentations: (1) Seminar at UNC-Greensboro, October 6, 1972, "Effect of Salinity and Temperature Upon the Ionic Regulation of the Blue Crab." (2) Spring 1972 at Myrtle Beach, South Carolina, Local Meeting of the Atlantic Estuarine Research Society, (3) Presentation at Columbia, South Carolina, "The rate of change in blue crab hemolymph conductivity after an abrupt salinity change" (University of South Carolina to the Comparative Biochemistry and Physiology Section of American Society of Zoologists, October 26-28). In addition to these presentations, the crab has been featured in newspaper articles and the popular press as well as being on display during various open houses at the Fisheries and to occasional visitors. Charles Nichols of NASA Langley Research Center, the developer of the electronic package, and Dr. Engel plan a publication in the Journal of Comparative Biochemistry and Physiology, an international journal reaching a large percentage of the marine biology community. Reaction and feedback from this publication is at least a year away, however.

Most likely the system is immediately adaptable to other crustacea larger than the blue crab (i.e., lobsters). To be more universally applicable, however, probably requires reduction in the probe size, as well as reduction in the entire transmitter package. In addition, some form fitting flexibility whereby the transmitting antenna can be molded to the back or other contour of the animal being evaluated would also contribute to its wide spread appeal. In this respect, a temperature compensated system would be highly desirable since data over the temperature range of 0°C to 40-50°C most assuredly will be required for meaningful environmental modeling in any marine species.
Additional useful properties would be for the system to be able to distinguish between various ions contributing to the ionic conductivity. Being able to separate the sodium contribution from the potassium contribution or that of other current carrying ions would make the probe a "dream" instrument. All or any of these features would contribute to its widespread acceptance.

The general ecological benefit to be derived, for the blue crab initially but ultimately for other crustacea and various fish species even, is the development of an estuarine productivity model. Such a model would enable marine biologists to predict the effect of both climatological changes and environmental pollutant burdens upon the survivability of a given species in an estuary. More importantly the combined effect of several independent changes could be carefully evaluated in a controlled laboratory environment. As such the lack of transmitting range of the present system is not a severe shortcoming (good thing, for electromagnetic wave propagation in sea water is not likely to be improved significantly in the foreseeable future). These studies will lead to a better understanding of estuarine waters and help explain the various fish or crab kills that have been reported in the past as well as provide the insight necessary to avoid their reoccurrence or even to anticipate their development in the first place.

Researchers at the Atlantic Estuarine Fisheries feel that the NASA instrument could play a very important role in solving such contemporary problems. The NASA system has not been engineered to the point where a commercial manufacturer will be willing to market it. Possibly with sufficient demand this eventuality will come to pass. While the workers at the Atlantic Fisheries are primarily researchers, they feel confident that many of their associates would welcome the opportunity to use a similar system in their own studies.
Consequently, the NASA monitoring system used on the blue crab could have an impact far beyond its limited sphere of influence to date. With some relatively modest modifications, such as temperature compensated circuitry, the system could be made more useful to Engel at the Marine Fisheries. With some serious engineering development, so as to include ionic probes and decal antennas, the system could become very powerful and widely used. The further development of this NASA system is a logical extension of space technology to marine and oceanography problems.

Recommendations

Because of the high potential impact of further development of the NASA blue crab monitoring system, RTI recommends further NASA technology utilization investment in this project. RTI recommends two steps: (1) immediate construction of a temperature compensated transmitter; (2) pending the interest generated by publicity to the existing program, the development of a well engineered, versatile, in vivo monitoring system for invertebrates in sea water suitable for widespread laboratory use.

The first task can probably be completed within a three to six month time span at a cost of between $5,000-$10,000 if carried out at Langley Research Center under the direction of Charles Nichols, supervising an RTI technician assigned to the task on a fulltime basis. This approach makes use of the same package style and technology, the same probe and same attachments as previously built and satisfactorily used. The only modification is to change the electronics so that the transmitter can operate over the temperature range between 0°C and 50°C with the calibration of the output as a function of temperature known to within ± 2%. Empirical calibration of the transmitter at different temperatures constitutes a perfectly satisfactory mode of operation so long as the transmitter is stable (does not drift by more than ± 2% in 24 hours). The intended operation of the system will be to operate the transmitter at a given temperature which will remain fixed throughout any given run. The option of being able to vary that temperature from the previously investigated 20°C is the only
additional freedom required. This means that the same transmitter and system can be used to gather data at 20°C one day and at 15 or 10°C the next. Eventually, the apparatus will be used in experiments in which both the salinity and the temperature of the water are simultaneously changed from known starting points to predetermined end points. Having a sensor to measure the crab's temperature at the same time would also be an additional useful input but this feature is not included as part of this procurement.

Dr. Engel at the Atlantic Estuarine Fisheries Center feels that the temperature compensated transmitter described above will be adequate to enable him to begin his long term program of determining the influence of pollutants upon the crab. This work will be extremely useful in ecological research and will attract the attention of other researchers working with other marine animals.

Dr. T. R. Rice, Director of the Atlantic Estuarine Fisheries Center has indicated that if hiring practices and support is available that the assignment of a technician to the task of gathering these data under the supervision of Dr. Engel would be made. The possibility exists of assigning even still another technician should the program warrant it.

The second step outlined above which calls for a reengineering of the sensor, the transmitting electronic package and the antenna is a full year engineering task best carried out by an instrument manufacturer or a manufacturer of commercial microelectronics (possibly a new, small business venture). Action over the next year by NASA TU should include bringing this opportunity to the attention of candidate producers and encouraging them to make whatever investments required. During this period feedback from the previously carried out experiments as well as the ongoing research at the Atlantic Estuarine Fisheries should become better known (because of increased publication and dissemination of results) and a more accurate determination of the economic potential and impact of the NASA monitoring system could be made.
APPENDIX F

LETTER FROM WILLIAM F. HERGET, EPA TO
JEFFREY HAMILTON, 16 NOVEMBER 1972 WITH COMMENTS ON:

- FCP-9, "Remote Instrument for Measurement of Exhaust Emission Flow Rate" and
- Remote Measurement of Particle Numbers and Size Distribution for Monitoring Smokestack Emissions."
Mr. Jeffrey Hamilton  
Code: KT  
NASA  
Washington, D.C. 20546

Dear Mr. Hamilton:

We have been asked by Mr. Robert M. Huffaker, NASA/MSFC, to comment on the relevancy to EPA interests of two particular tasks that he has submitted to your office. The tasks are:

1. "Remote Instrument for Measurement of Exhaust Emission Flow Rate;" and  
2. "Remote Measurement of Particle Numbers and Size Distribution for Monitoring Smoke-Stack Emissions."

Both of these tasks are quite relevant to the interests of the Stationary Source Emission Measurements Section since present and future emission standards require measurement of pollutant emission rates. In fact, we funded the fabrication of a laser velocimeter for in-situ measurement of stack gas velocities during FY '72. This instrument is based on the dual-beam laser velocimeter technique which has been studied in considerable detail for the Air Force at Arnold Engineering Development Center. We are presently funding work at AEDC for the application of the dual-beam technique to particle size determination.

It is doubtful that the present modest expenditure of EPA will completely solve the problems of remote velocity and size distribution measurements. Our limited resources and other activities of higher priority do not permit us to support this effort to any greater extent than our present involvement. Because of the relevancy of the proposed activity to the work we are already supporting, any effort that NASA can bring to bear on the problem with its resources will certainly complement our program and be of considerable value and interest.

Sincerely,

William F. Herget
Division of Chemistry and Physics

cc: Mr. Robert Donovan  
Research Triangle Institute
APPENDIX G

LETTER FROM CHARLES EASTWOOD, NASA HEADQUARTERS

TO MARVIN H. BROWN, MSFC, 27 NOVEMBER 1972

WITH THE FOLLOWING ATTACHMENTS:

(1) Letter from Marvin H. Brown, MSFC, to Jeffrey Hamilton, NASA Headquarters, 14 November, 1972,
(2) Letter from C. W. Moody, Alabama State Forester to James W. Wiggins, MSFC, 19 October, 1972, and
(3) Draft proposal, Forest Fire Detection and Location.
TO: Marshall Space Flight Center  
Attn: Mr. Marvin H. Brown  
DIR/A&PS-TU  

FROM: KT/Director, Technology Utilization Office, Office of Industry Affairs and Technology Utilization  

SUBJECT: Up-dated Proposal:  Forest Fire Detection and Location System  

We have your letter of November 14th to Mr. Jeffrey T. Hamilton indicating the change in your proposal for a Forest Fire Detector, and requesting funding information.  

Mr. Frank Ayers of the Research Triangle Institute is assisting us in coordinating efforts of Ames Research Center and Marshall Space Flight Center with the Alabama State Forestry Commission.  

We view this opportunity favorably but would like clarification of the Alabama Forestry Commission position. Apparently they have not seen a proposal from you, and have one from Ames.  

It would be useful to know how this work fits into efforts of the U.S. Forestry Service in remote sensing for forest fire control. Herewith is the blue binder containing summaries of the materials presented at the U.S. Forestry Service Conference on Fire Detectors. The loan of the material is very much appreciated.  

Charles R. Eastwood  
Technology Utilization Office  
Office of Industry Affairs and Technology Utilization  

Enclosure  

cc: KT/J. T. Hamilton  
RTI/Frank Ayers
TO: NASA Headquarters  
Attn: KT/Jeffrey T. Hamilton  

FROM: A&PS-TU-DIR/Marvin H. Brown  

SUBJECT: Updated Proposal: Forest Fire Detection and Location System  

As you will note from the enclosed letter from the Alabama Forestry Commission, they are still very interested in participating in this project. Under the personnel and funding limitations now in effect, MSFC is no longer in the position of being able to develop a complete prototype system based upon the panoramic scanning technique. Instead, as noted in the attached draft proposal, MSFC suggests that a systems analysis approach be used to determine the basic characteristics of a system which will meet the Forestry Commission's requirements. Maximum utilization will be made of MSFC equipment and facilities to simulate various types of displays and data links. The proposal is still in the draft stage and may be modified in response to Forestry Commission requirements and according to the priority given to the project.

Considerable work is involved in the scheduling of MSFC manpower and resources to support each new project, so we have decided not to seek MSFC management approval until we receive a definite decision as to if and when the project is to be funded.

We must ask for the return of the blue binder containing the summaries of the material presented at the U.S. Forest Service conference on fire detection. The information will be used during the initial study phase of the project.

Marvin H. Brown  
Assistant Director, Technology Utilization  

Enclosures  

cc: KT/Charles Eastwood
October 19, 1972

Mr. James W. Wiggins
Marshall Space Flight Center
Huntsville, Alabama 35812

Dear Mr. Wiggins:

This will confirm parts of our conversation this morning concerning the desirability of proceeding with the development of an automated fire detection system. I am real excited by the prospects described and assure you that the Forestry Commission will participate to the maximum we can with our limited resources.

As I stated, we cannot assume any financial responsibility in this project due to limited funds, but will make Commission equipment, facilities and personnel available as needed and compatible with our other duties and responsibilities. Mr. Richard Cumbie who is our District Forester with headquarters in Huntsville and whose address is 528 Courthouse, Huntsville 35801, telephone number - 536-5911, Ext. 246 & 247, will act as our representative and local contact in this project. The overall technical responsibility rests with Mr. H. C. Lucas, Director of the Forest Resource Protection Division in Montgomery.

Please call on either of the above or myself if we can be of further help to you in this matter. I appreciate your agency assuming responsibility in this particular sphere of civilian resource protection matter and look forward to working with you.

Sincerely,

C. W. Moody
State Forester

cc: Mr. H. C. Lucas

Mr. Richard Cumbie
SUBJECT: Forest Fire Detection and Location

It is proposed that the MSFC Astronics Laboratory assist the Alabama Forestry Commission in a systems analysis and design study to determine whether video scanning techniques may be adapted to the remote detection and location of forest and range fires. The limited amount of work done in this area by other groups will be reviewed and used as a starting point for system considerations. Sufficient equipment will be assembled to test the basic design philosophies developed and to determine the basic characteristics of a system which will satisfy the Forestry Commission's requirements. The tests will simulate the various types of displays and data transmission links and will provide a basis for comparisons of commercial systems as they become available.

The study will be closely coordinated with the representatives of the Alabama Forestry Commission.
Background

This project first originated as the result of discussions between Mr. Larry McLennan, Alabama Forestry Commission, and representatives of the MSFC Technology Utilization Office. A need existed for a remote, unattended means of identifying and locating forest and brush fires early enough for fire crews to be able to reach and control the fires before extensive damage occurred. A network of fire towers connected by telephone lines exists throughout the region, but the towers are not always manned except during fire emergency situations. It was evident that a simple system was required that could function largely without attention, yet which could provide useful information to central monitoring stations supervising large areas where manned towers might not be available at all times.

MSFC had been investigating the use of a miniature panoramic scanner and it appeared that the technique could be adapted to the problem at hand. The type of scanning was adaptable to the slow information transmittal rates possible with telephone transmission lines, and there was the possibility that the system could also act as an infrared (IR) detector to give an alarm in case a fire or heat source were detected, then shift to a visual scanning mode to assist in the positive identification and location of the anomaly. It was proposed that the existing system be utilized to determine broad design parameters and that a unit be fabricated and tested at MSFC, under the
guidance of the Forestry Commission representative. The scanning system also had potential applications in urban fire detection and traffic control situations, so would have been tested in a variety of locations and applications in the Huntsville area. The design and fabrication would have been accomplished within MSFC and the testing and overall program direction would have been the responsibility of the TU Office.

However, since the proposal was first prepared, Mr. Bulette (one of the principal instigators of the project) has retired, there have been substantial cutbacks in both NASA and contractor employee strength, and considerable redirections of effort within MSFC. In addition, the original panoramic scanner is no longer available for the necessary preliminary tests.

Comment

The subject of detecting and locating such fires is critical and a considerable amount of work has been done to devise and test various techniques, systems, and concepts. However, it appears that the work has been largely uncoordinated and has been hampered by a lack of either definite statements of requirements or of any standardized tests which could be used to compare the relative merits of the various approaches. Even if the proposed MSFC/Alabama Forestry Commission effort does nothing else, the establishment of guidelines and a systematic test program should be of significant value.
Approach

I. Headquarters/KT and MSFG management must assign some priority to this project and determine if resources and personnel are available to accomplish the agreed upon statement of work within the specified time frame. The statement of work should be specific and must be developed after a review has been made of past and present research and development in the forest fire detection field.

II. A systems analysis approach will be taken during the first phase of the project. A review will be made of past and on-going research and development and a careful analysis made of the required and/or desirable features to be incorporated in a fire detection and locating system. Specific attention will be given to determining methods of display and data transmission since these parameters determine certain features of the scanners to be investigated.

A set of basic detection and location factors will be agreed upon, such as range, angular discrimination, resolution, atmospheric constraints, types and sizes of events to be detected and the allowable thresholds for each, etc. It is possible that a series of standard test fires or equivalent may be established for use in the comparison of various types or styles of competing fire detection systems. Such standards do not apparently exist at this time, so the evaluation of such systems must be largely a subjective matter at best.
III. A determination will be made of the best approach to the establishment of the test range. Possibilities include placing the remote instrumentation at or near the MSFC Astrionics Laboratory or at an existing Forestry Commission fire tower equipped with telephone and electrical power outlets.

It will be necessary to obtain a means of data transmission between the remote instrumentation and the MSFC Astrionics Laboratory. Coaxial cable will be used for short distances, and a microwave link for distances greater than one-half mile. In addition, a telephone-based command system (MODEM) will be obtained for control of the remote instrumentation and return of narrow band data from the remote site during the test and evaluation phases.

A data terminal will be established within the MSFC Astrionics Laboratory so that available instrumentation and equipment may be used to simulate a variety of data transmission and display techniques. Such a simulation is felt to be desirable since it is under the control of the experimenter and can be readily converted from one mode to another for comparative purposes. For example, existing data conversion equipment is available to simulate slow-scan versus real-time visual transmission. It may also be possible to test various types of detection and alarm circuitry should such be found desirable during the systems analysis portion of the study. Interaction of various types of video and graphical displays may be studied as well.
IV. The remote scanner configuration cannot be determined at this time. However, several approaches have been proposed and will be considered during the initial systems analysis phase and, where possible, will be actually assembled and tested. The purpose of the test is not to qualify any one particular device, but rather to determine the optimum parameters of a device which could be constructed to meet the Forestry Commission specifications and requirements.

The initial tests will be based upon the use of readily available equipment operating in the visible portion of the spectrum. If time and funds permit, additional tests will be made using wave length filters and image converter tubes to determine their suitability to the problem at hand.

The preliminary discussions have identified at least three approaches which will be considered.

a) Mechanical Scanners -

The prototype panoramic scanner is no longer available for tests and it was considered too expensive to construct a second scanner until other tests had identified the operating parameters of the detection and location system. Simulation of this type scanner will be provided for comparison.

b) Video Scanner - Conventional Image

The most common concept is the use of a horizontally mounted video camera arranged so that it can rotate to various azimuths and which
contains some form of variable focal length lens and/or a filter system. Such a system is fairly bulky and has a number of mechanical and electrical features which would cause maintenance and reliability problems.

It is proposed instead that the video camera be mounted in a vertical position so that various imaging and scan techniques may be tested with the same video unit.

The panning motion of a conventional image may be simulated through the use of a Dove prism mounted in a vertical position above the video scanner. The construction of the prism is such that a vertical (conventional) image is seen as the prism is rotated through the 360° horizontally. The motion will be controlled so that the operator can view a series of stationary images or a slowly moving image, as desired. The actual video signal will be converted to simulate either real-time or a variety of slow-scan data transmission modes for testing and evaluation.

c) Video Scanner - Unconventional Image

Depending upon the results of the systems analysis and prior tests, nonconventional scanning systems may be considered. As one example, instead of a "panning" or other visual scanning motion being employed, it is possible to place a conical reflecting surface over the video scanner so that the complete 360° field may be viewed at once. The image will resemble the
PPI (plan-position-indicator) display of a radar set in that the remote viewing site would be located at the center of the display, and the horizon would lie around the periphery of the display. Azimuth and possibly range information is immediately available from such a display, but there is the counter question as to whether the image might be too confusing to an unskilled operator.

V. At the conclusion of the testing and evaluation phase, a careful study and analysis should identify the basic characteristics and parameters which must be met by the final fire detection and location system - with recommendations regarding the leasing or purchase of various portions of the system.

VI. Since there is the possibility of considerable time being required to develop certain portions of the ultimate system, MSFC cannot at this time agree to undertake the design and fabrication of the final system. However, technical consultation and advice may be provided where possible and the test facility can be made available for comparative testing and evaluation of the completed system or subsystems (on a time and facility available basis).
Schedule

The project must be accomplished on a noninterference basis with ongoing MSFC projects so the actual time and personnel assignments will be dependent upon the priority assigned. Maximum utilization will be made of available MSFC equipment and facilities but these cannot remain dedicated to a long-term testing program. With the proper priority, the assembly of hardware and the testing could be accomplished within a period of about one month. This would be dependent upon the prior availability of the data transmission and control installation, and upon the availability of the results of the systems analysis and design study which should have defined the test parameters and goals.

Funding

No precise estimate of the funding can be given because of the developmental nature of the project. It is estimated that approximately $10,000 will be required to obtain a microwave data transmission system and the MODEM control installation. Approximately $15,000 would be devoted to the purchase or fabrication of various items to obtain specific information during the test, rather than to obtain hardware items for the ultimate system. The basic installation at MSFC will be at essentially no cost since the items will be "lent" to the project from existing programs.
APPENDIX H

LETTER FROM H. C. LUCAS, ALABAMA FORESTRY COMMISSION,

TO FRANKLIN A. AYER, RTI, 22 NOVEMBER 1972,

EXPRESSING SUPPORT FOR THE DEVELOPMENT OF A

FOREST FIRE DETECTION SYSTEM.
Mr. Franklin A. Ayer  
Research Triangle Institute  
P. O. Box 12194  
Research Triangle Park, North Carolina 27709

Dear Mr. Ayer:

Reference is made to the letter from State Forester C. W. Moody to you October 24, 1972, regarding the need and support by the Alabama Forestry Commission in the development of a remote forest fire detection system.

One of the Forestry Commission's greatest needs at the present time is a better and more dependable way to detect forest fires and detect them while they are small. Our objective is to discover all such fires within ten minutes after ignition.

Our present detection system is made up of 150 lookout towers located in strategic places over the state. This system is not satisfactory for a number of reasons. A few of the reasons are: lack of visibility during times of haze and smoke; unable to employ personnel that will operate the towers in remote areas; shortage of qualified personnel in many parts of the state; unable to man during weather.

We are very much interested in the detection possibilities offered by remote sensing or any other mechanical detection system that will provide us with the necessary tools to do an adequate job in detecting and locating forest fires. Such a system, however, should be moderately priced and economically feasible in operation.

I have reviewed both systems covered by the enclosures and it is my opinion that it would be to our best interest to go with a system produced by the Marshall Space Flight Center. Other recommendations regarding the system is that it be operated from a tower or stationary location and simple enough to permit operation by non-technical personnel of the Forestry Commission.
As stated in Mr. Moody's letter to Mr. Wiggins at the Marshall Space Flight Center, we do not have funds available to apply on such a project but if you should begin work on the project, we could provide certain facilities, Commission equipment, and personnel in the demonstration and evaluation phase of the system.

Please advise if you need additional information or if we can be of help to you in this matter.

Sincerely,

H. C. Lucas, Director
Forest Resource Protection Division

HCL/vn

cc: Mr. C. W. Moody
    Mr. Richard Cumbie
APPENDIX I

LETTER FROM FRANKLIN A. AYER TO H. C. LUCAS,

ALABAMA STATE FORESTRY COMMISSION

29 NOVEMBER 1972 AND FORWARDING TO HIM

MSFC'S UP-DATED PROPOSAL (APPENDIX F)
Mr. H. C. Lucas, Director
Forest Resource Protection Division
Alabama Forestry Commission
513 Madison Avenue
Montgomery, Alabama 36104

Dear Mr. Lucas:

Reference is made to your letter to me dated November 22, 1972, a letter from State Forester C. V. Moody to me dated October 24, 1972, and my letter to State Forester Moody dated October 17, 1972.

I was delighted to receive your letter expressing support from the Alabama Forestry Commission in the development of a remote forest fire detection system. I'm also glad that you have reviewed the proposals made by MSFC and ANDROS, Inc. Since your review, however, I have received an up-dated draft of the MSFC proposal which indicates that MSFC, due to personnel and funding limitations, is no longer in a position of being able to develop a complete prototype system based upon the panoramic scanning technique. Instead, as noted in the attached proposal, MSFC suggests that a systems analysis approach be used to determine the basic characteristics of a system which will meet your requirements.

In view of the fact that you feel that it would be to your best interest to go with the original system suggested by MSFC, I would like to request that you review MSFC's up-dated proposal to see if your ideas remain the same.

I'm glad to report that personnel at NASA Headquarters continue to view favorably this opportunity to assist you in solving one of the Forestry Commission's greatest needs -- to detect fires and detect them while they are small.

Please advise if I can be of further assistance to you.

Sincerely,

Franklin A. Ayer, Manager
Environmental Technology Department

cc: Mr. C. W. Moody, Alabama State Forestry Commission
Mr. Marvin H. Brown, MSFC
Mr. Charles R. Eastwood, NASA Headquarters
Mr. David J. Winslow, MSFC

Enc.: 1
APPENDIX J

LETTER FROM FRANCIS POOLER, JR., NOAA,
RESEARCH COORDINATOR, REGIONAL AIR POLLUTION STUDY,
EPA, 3 NOVEMBER 1972 TO R. P. DONOVAN, RTI.

SUBJECT: Review by Dr. Pooler of Colorado State University's Proposal.
Mr. R.P. Donovan
Center for Technology Applications
Research Triangle Institute
P. O. Box 12194
Research Triangle Park, North Carolina 27709

Dear Mr. Donovan:

I read through the proposal concerning an acoustic radar from Dr. R. J. Churchill of Colorado State University, and have briefly discussed it with a couple of other meteorologists here. We would give this proposal in its present form a rather low priority for support, for two principal reasons.

(1) There is only the sketchiest information to indicate what equipment configuration is proposed, and how it would be operated. Hence, one cannot judge if there really is anything proposed that has not been done elsewhere already. Operation in the sweep frequency mode is a new idea to me, but I couldn't get a good enough description from the proposal to be able to even guess at operating limitations which might be encountered.

(2) It is not clear what use would be made of such a system if it were developed. There are occasions when the signal returned from the atmosphere is too weak to be of any use; it is not clear from the proposal that this fact is recognized, or whether it is being glossed over.

I would suggest, if Dr. Churchill cares to, that a more complete proposal be prepared, in which more details of instrumentation and proposed operation of the system be given. If such is done, I'd suggest that an opinion from the NOAA Wave Propagation Laboratory on the instrumental aspects be obtained; that group is far more qualified than we are to evaluate the hardware.

Sincerely yours,

Francis Pooler, Jr., NOAA
Research Coordinator
Regional Air Pollution Study

cc: Dr Hall
APPENDIX K

November 20, 1972

Dr. Richard Thompson
Chief, Air Quality Analytical Branch
EPA, NERC
Research Triangle Park, North Carolina 27711

Dear Dick:

I am enclosing a reprint of the NASA Lewis memorandum we discussed last week. This copy also contains the FTS number for Davis and Graab as you requested.

Sorry it took as long as it did, but I had to obtain an additional copy from Headquarters myself.

Sincerely,

\[\text{Bob}\]

R. P. Donovan

RPD:bcb
Enclosure
A RAPID PROCEDURE FOR DETERMINATION OF NICKEL, COBALT, AND CHROMIUM IN AIRBORNE PARTICULATE SAMPLES

by Warren F. Davis and Judson W. Graab

SUMMARY

This memorandum describes a rapid procedure for the determination of 1-20 micrograms nickel, chromium and cobalt in airborne particulates collected in the powder metals laboratory.

Previously used methods for determining trace metals in airborne particulates, such as colorimetric analysis, emission spectroscopy or neutron activation analysis, were judged either as too slow or the instrumentation was too complex and/or not available. This procedure was developed to satisfy a need for a rapid, selective, and sensitive method for determining the above three metals.

The method described utilizes the combined techniques of low temperature ashing (LTA) and atomic absorption spectroscopy (AAS). The airborne particulates are collected on analytical filter paper by means of diaphragm pumps. The filter papers are quickly and completely ashed at low temperature in a 10-ml beaker in a stream of electronically excited oxygen. The residues are dissolved in hydrochloric acid and nickel, chromium and cobalt are determined directly without transfer with good precision and accuracy by means of atomic absorption. Speed and convenience are increased by use of a dual channel instrument, permitting simultaneous measurement of two elements, and the use of the same flame conditions for all three elements. Since no separations, filtrations or transfers of solutions are required, the procedure is rapid.
TECHNICAL MEMORANDUM

A RAPID PROCEDURE FOR DETERMINATION OF NICKEL, COBALT, AND CHROMIUM IN AIRBORNE PARTICULATE SAMPLES

by

Warren F. Davis and Judson W. Graah

ABSTRACT

A rapid, selective procedure for the determination of 1-20 micrograms nickel, chromium and cobalt in airborne particulates is described. The method utilizes the combined techniques of low temperature ashing and atomic absorption spectrometry. The airborne particulates are collected on analytical filter paper. The filter papers are ashed and the residues are dissolved in hydrochloric acid. Nickel, chromium and cobalt are determined directly with good precision and accuracy by means of atomic absorption. The effects of flame type, burner height, slit width and lamp current on the atomic absorption measurements were studied.
Recovery of weighed amounts of nickel, chromium, and cobalt powders was 92-100 percent complete. The effects of flame type, burner height, slit width and lamp current on the atomic absorption measurements were studied. A moderately rich acetylene-air flame was selected for measurement of the three elements because each exhibits good sensitivity with this condition. Interference effects which may dictate the use of an oxidizing flame for the determination of nickel and cobalt were absent.
INTRODUCTION

A survey (ref. 1) was conducted in 1966 by Viles, Chamberlin, and Boylen to obtain information on the toxicological properties and to investigate methods for the analytical determination of certain metals and metal oxides used in the Lewis Research Center powder metals laboratory. The materials studied included the following: nickel, tungsten, thorium oxide, aluminum and aluminum oxide, magnesium oxide, zirconium oxide, niobium, molybdenum, cobalt, and chromium. Special emphasis was placed on the influence that extremely small particle sizes, 0.002 to 0.03 micrometers (20-300 Å), may have on the toxic hazard of exposure to many metals or metal oxides.

A lack of information concerning the physical, chemical and biological behavior of metal particles in the ultrafine size range required that a conservative view be taken when estimating the potential toxicological hazard of these metal powders. The suggested maximum airborne particle concentrations are merely estimates of what is believed would provide reasonable assurance of safety to the health of employees. The report recommended a threshold limit value (TLV) of 0.002 mg/m$^3$ for cobalt, chromium, and nickel. This
TLV for nickel as ultrafine powder particles is the same as that recommended in 1966 by the American Conference of Governmental Industrial Hygienists (ACGIH) for nickel carbonyl. As late as 1971, ACGIH had set no limits for cobalt, chromium, and nickel particles of less than 0.3 micrometers.

Colorimetric or neutron activation methods of analysis were used by Viles, et al., for determining all the metals but thorium which was measured by its alpha decay rate.

It was concluded (ref. 1, p. 7) that nickel, cobalt, chromium, and thorium were the most hazardous of the materials studied. Nickel, cobalt, and chromium are also among the most widely used metals at Lewis Research Center as many high-temperature alloys are based on them. Thorium is dispersed in small amounts in certain alloys to increase strength.

As a result of the recommendations of the above report, a surveillance program was instituted. Airborne particulate samples were taken at operator positions near ball mills, ultrasonic cleaners, attritors, blenders, dry boxes, and hoods. Samples were also taken at building exhausts. High efficiency particulate air (HEPA) filters were installed in all exhausts. A HEPA media has a minimum efficiency rating of 99.97 percent for 0.3 micrometer particles (ref. 2) as determined by the dioctyl phthalate (DOP) test method at airflows of 20 and 100 percent of the rated flow capacity of the filter assembly. Sampling of the exhausts would detect failure of the HEPA filters and possible contamination of the immediate area.
Atmospheric contamination outside the building was proven to be negligible.

Methods frequently used for determining trace metals in airborne particulates, such as colorimetric analysis, emission spectroscopy or neutron activation analysis were judged either as too slow or the instrumentation was too complex. The procedure described below, utilizing low temperature ashing (LTA) and atomic absorption spectroscopy (AAS), has the advantages of speed, selectivity and sensitivity. AAS has been applied recently to the analysis of toxic metals in samples of airborne particulates (refs. 3-6).

Rapid analysis of samples is necessary in order to be able to locate and correct an unsafe condition promptly. In the procedure described, air particulate samples are collected on filter papers, ashed at low temperature, and the residues are dissolved in acid. After dilution, the solutions are analyzed for nickel, chromium, and cobalt by AAS. Since no separations, filtrations, evaporations, or transfers of solution are necessary, 20 samples may be analyzed for the three elements in two hours.

EXPERIMENTAL WORK

A. Sample Collection

Following the recommendations of the survey by Viles, et al., 2.5-cm Whatman 41 filter paper was adopted as the collection medium. Glass fiber filters contain significant amounts of many elements including nickel and chromium (ref. 3). The high concentration of soluble salts causes a significant matrix effect (ref. 5). Upon
treatment with a mixture of hydrochloric and hydrofluoric acids, the resulting semi-dissolved solids were observed to decrease the aspiration rate and sometimes plug the plastic aspiration tubing leading to the nebulizer of the atomic absorption spectrometer. Use of Whatman 41 ashless filter paper eliminates the plugging problem, lowers the blank, and avoids the matrix effect of the glass fiber filters.

A paper by Dams, et al, (ref. 7) published after this work was completed has evaluated various filter materials for suitability for atmospheric particulate sampling and eliminated analysis by neutron activation. It was concluded that of commercially available filters, Whatman 41 is optimum from the standpoints of low blanks, particle retentivity, and ease of handling.

Samples were collected on 2.5-cm Whatman 41 filter papers supported by filter funnels. An air flow was supplied by electric diaphragm pumps. The pumps were started and stopped by individual electric timers. Samples were collected only during working hours. The sampling time was 40 hours and the volume of air, measured by a gas meter, was usually 10-20 cubic meters.

Areas where samples were collected include the following: A work bench, an attritor hood, a dry box air lock, a powder weighing area, four blowers with HEPA filters, two hydrogen cleaners, a roof vacuum pump exhaust, a hood for radioactive materials, a machine shop grinding area, and three exhaust manifolds.
B. Sample Ashing

The use of the low temperature ashing technique for the treatment of air sample filter papers appeared to offer several advantages over conventional wet ashing with mineral acids or dry ashing in a muffle furnace at about 500°C. These include speed, convenience and less chance of contamination or loss. Acids are a possible source of contamination and a carbonized residue remains. Ignition in a furnace may cause contamination from the container or atmosphere and certain elements may be volatilized or converted to refractory compounds. The use of a low temperature asher (refs. 8 and 9) avoids most of the disadvantages cited above and is faster as well.

In this work, a Tracerlab Model LTA-505 low temperature asher was used to quickly and completely ash the filter paper samples. Five samples can be ashed simultaneously at relatively low temperature by electronically excited oxygen without danger of contamination (ref. 10). In the case of very volatile elements, e.g., mercury, selenium, and arsenic, losses may be significant (ref. 8). The asher is illustrated schematically in figure 8.

Oxygen flows into a common inlet manifold, and at reduced pressure and low flow rate, passes down through five separate vertical tubes surrounded by a rf coil. The coil generates a high frequency electromagnetic field in which molecular oxygen is converted to excited, very reactive atomic and ionic species. This mixture flows through horizontal oxidation chambers containing the samples.
Volatile products of combustion and excess oxygen are drawn into an exhaust manifold and removed by a vacuum pump. The actual temperature reached by the sample depends on such factors as the thermal conductivity and specific heat of the sample, the concentration of excited oxygen available and whether the chemical reaction is exothermic or endothermic. The concentration of excited oxygen is directly controlled by the power input to the rf coil, and to some extent, by the flow rate and pressure of the molecular oxygen entering the system. Ashing rate is affected by the sample temperature, the amount of surface area exposed, and the inorganic content of the sample. The time required to completely ash a 2.5-cm filter paper disc was observed to vary with the amount of particulate matter it contains and also its orientation in the stream of electronically excited oxygen. Oxidation is most rapid when the paper is upright in a 10-ml beaker. Ashing is usually complete in 10 to 15 minutes.

C. Sample Solution

The metallic residues are heated gently in covered 10-ml beakers with 0.25-ml 12 M hydrochloric acid for 10 to 15 minutes. Finally, the clear solutions are diluted with 10-ml 1 \text{V/o} hydrochloric acid added by buret. The beakers are covered and warmed briefly to obtain mixing.

D. Sample Measurement

The concentrations of the three elements in the solutions are determined by atomic absorption spectroscopy. The instrument used
to obtain the absorption measurements was an Instrumentation Labora-
tory Model 153 atomic absorption spectrophotometer (ref. 11). This
instrument is manufactured with two double beam optical channels.
In one channel (Channel A), there is a 1/3 meter Lébert grating mono-
chromator with 1200 lines/mm, and in the other (Channel B), an inter-
ference filter is used for wavelength selection. Nickel and cobalt
are determined in Channel A at 232.0 and 240.7 nm, respectively, and
simultaneously, chromium is determined in Channel B using a 357.9 nm
interference filter monochromator. Single element high intensity
hollow cathode lamps were used for each element. A boiling three-
slot laminar flow burner with a rich acetylene-air flame was used
for all the measurements. Variable scale expansion is available in
each channel. The instrumental parameters used for the measurements
are listed in Table II.

After making blank corrections, the concentrations of nickel,
cobalt and chromium were calculated by comparison with measurements
of standard solutions of the metals in 1 V/o hydrochloric acid.

RESULTS

A. Recovery Experiment

Experiments were performed to determine the recovery of nickel,
cobalt and chromium using the procedure described. About 1 mg
amounts of each of the finely divided metals were weighed on a Met-
tler Micro Gram-atic Balance into 10-mL glass beakers. A 2.5-cm
Whatman 41 filter paper disc was placed upright in the sample beakers
and in blank beakers. The papers were ashed at maximum rf power with
the oxygen flow adjusted to about 50 cc/min. A chamber pressure of about 1 mm mercury was maintained by the oxygen flow. Slow pumping rates and pressure changes were used to avoid disturbing the finely divided metals.

The metal residues were dissolved by heating with small amounts of 12 M hydrochloric acid. The solutions were diluted to 100-ml with 1% hydrochloric acid and then aliquots were further diluted so that the metals were in the concentration range of about 0.5 to 1.7 ppm. Finally, the recovery of the three metals was determined by comparison of their atomic absorption measurements, using the parameters in Table II, with those of standards prepared from the same metals. The results of the recovery experiment are tabulated in Table I. A recovery of 92 to 100 percent is considered satisfactory at this level and gives confidence in the precision and accuracy of the procedure.

B. Effect of Instrumental Parameters on Sensitivity

Calibration curves for nickel, chromium, and cobalt are given in figures 1, 2, and 3. In the cases of nickel and cobalt, the variation of sensitivity with slit width is shown. Since chromium is determined in channel B using an interference filter, the effect of slit width on this element is not shown. Higher sensitivity is obtained for nickel and cobalt with a 0.001 micrometer slit width than with a wider setting. However, the main reason for the use of a narrow slit were references in the literature (refs. 11 and 12) to the presence of nonabsorbing lines (231.7, 232.1, and 240.77 nm) close
to the nickel and cobalt absorption lines 232.0 and 240.72 nm. The absorption lines used for these two elements are the most sensitive available, but a narrow bandpass is necessary. A decrease in the slit width results in an increase in sensitivity but at the expense of a noisier signal (ref. 11).

The effect of hollow cathode lamp current on the sensitivity of absorption by nickel, chromium, and cobalt is indicated in figure 4. Both nickel and cobalt show decreases in absorption with an increase in lamp current but chromium absorption is unchanged.

The effects of burner height and type of flame on absorption by nickel, chromium, and cobalt are shown in figures 5, 6, and 7. Burner height is the distance from the top of the Boring burner to the horizontal beam of the hollow cathode lamp. A lean flame and an increase in burner height results in the poorest sensitivity for all three elements. Because it forms a stable monoxide (ref. 13), chromium shows the largest increase in sensitivity as the flame is made richer. Chromium has a three-fold higher sensitivity in a moderately rich flame than in a lean flame. A burner height of 10 mm and a slightly luminous flame was adopted for all measurements as this was convenient and nearly optimum for all three elements. The desired degree of luminosity can be reproduced more easily by visual observation than by a fuel/air pressure ratio. In these samples, significant interferences are absent. Generally, however, an oxidizing nonluminous flame is used for nickel and cobalt (ref. 11).
C. Size and Variation of Blank

Blank determinations are made by taking 2.5-cm Whatman 41 filter paper discs through the ashing, dissolution and measurement steps exactly as for samples. A total of 12 blank determinations performed on five days, calculated to the equivalent amount of nickel, chromium and cobalt, were as follows:

<table>
<thead>
<tr>
<th></th>
<th>Nickel</th>
<th>Chromium</th>
<th>Cobalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average blank, µg</td>
<td>0.18</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>Standard deviation, µg</td>
<td>0.09</td>
<td>0.08</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**CONCLUDING REMARKS**

A relatively simple and rapid procedure has been described for determination of 1-20 micrograms nickel, chromium, and cobalt in airborne particulate samples. The procedure combines the advantages of LTA and AAS and requires a minimum amount of handling.

The use of these techniques makes possible the analysis of 20 samples in two hours. If any of the three elements are found to exceed the TLV at any station, appropriate action may be taken quickly. The lack of interferences and high sensitivity make possible the measurement of all three elements in one solution with a single set of flame conditions.

Use of analytical grade filter paper for sampling and the low temperature asher for oxidation require less time and less acids than wet ashing. Also, there is less chance of contamination, volatilization loss or conversion to refractory compounds than in ashing in a muffle furnace at 500° to 550°C.
The use of filter paper and the LTA instead of glass fiber filters and acid leaching result in a clear solution with a low blank, no carbonaceous residue requiring separation and no semi-dissolved solids to cause a matrix effect and plugging of the aspirator tubing.

The recovery of nickel, chromium and cobalt metals is 92 to 100 percent complete. This is considered satisfactory in the 0.2 to 1.0 ppm range and gives confidence in the precision and accuracy of the procedure.

Variation of sensitivity of the three metals as a function of slit width, lamp current, burner height, and flame type was studied. A moderately rich acetylene-air flame was selected to optimize sensitivity for chromium but it was also found very satisfactory for nickel and cobalt since interferences were absent. Sensitivity decreases slightly with increasing burner height. Nickel and cobalt show decreasing sensitivity with increasing lamp current but the sensitivity of chromium is constant. Sensitivity in channel A is an inverse function of slit width. Use of a narrow slit is recommended due to nonabsorbing lines being close to the most sensitive nickel and cobalt lines. This results in a slightly noisier signal but calibration curves are linear. Calibration with standards is done with each set of samples to compensate for slight variations in instrumental operating conditions.
APPENDIX A

Equipment and Chemicals

1. Atomic absorption spectrophotometer with two double beam optical channels, such as IL Model 153 (Instrumentation Laboratory, Inc., Lexington, Mass.).

2. Low temperature asher, such as LTA-505 (LFE Corporation, Waltham, Mass.).

3. Diaphragm pumps, Model 8T-012 (Universal Electric Company, Owosso, Mich.).

4. 2.5-cm Whatman No. 41 ashless filter paper.

5. Stock solutions; 10,000 ppm of nickel, chromium, and cobalt.

6. Hydrochloric acid, 12 M and 1 V/o dilution.

Procedure

1. Air filter samples and blank filter papers are placed upright in 10-ml glass beakers. These beakers are placed in trays in the individual chambers of the LTA. The LTA is operated according to the manufacturer's recommendations.

2. After ashing, add to the residues in the beakers 0.2 to 0.4-ml of 12 M HCl, then cover and heat briefly (15 to 20 minutes).

3. Add 10 ml 1 V/o HCl to the beakers, cover and warm for approximately 10 minutes to obtain mixing.

4. Atomic absorption measurements of nickel, chromium and cobalt are made using the parameters listed in Table II.

5. Standards and blanks are run with each set of samples to compensate for slight changes in sensitivity resulting from not exactly reproducing the desired instrumental conditions. After
making blank corrections, concentrations of the three elements are calculated by comparison with measurements of standard solutions of the metals diluted with 1%/ HCl. Results are calculated as milligrams metal per cubic meter of air sampled.
# Appendix B

## Table I - Recovery of Nickel, Chromium, and Cobalt After Low-Temperature Ashing

<table>
<thead>
<tr>
<th>Metal</th>
<th>Weight, mg</th>
<th>Ppm Added*</th>
<th>Ppm Found</th>
<th>Percent Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>1.010</td>
<td>0.50</td>
<td>0.49</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td></td>
<td>0.98</td>
<td>97.0</td>
</tr>
<tr>
<td></td>
<td>1.100</td>
<td>0.55</td>
<td>0.53</td>
<td>96.4</td>
</tr>
<tr>
<td></td>
<td>1.10</td>
<td></td>
<td>1.01</td>
<td>91.8</td>
</tr>
<tr>
<td>Chromium</td>
<td>1.720</td>
<td>0.86</td>
<td>0.80</td>
<td>93.0</td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td></td>
<td>1.60</td>
<td>93.0</td>
</tr>
<tr>
<td></td>
<td>0.960</td>
<td>0.48</td>
<td>0.46</td>
<td>95.8</td>
</tr>
<tr>
<td></td>
<td>0.96</td>
<td></td>
<td>0.92</td>
<td>95.8</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.580</td>
<td>0.58</td>
<td>0.55</td>
<td>95.0</td>
</tr>
<tr>
<td></td>
<td>0.58</td>
<td></td>
<td>0.57</td>
<td>98.6</td>
</tr>
<tr>
<td></td>
<td>0.775</td>
<td>0.775</td>
<td>0.77</td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>0.775</td>
<td></td>
<td>0.77</td>
<td>98.8</td>
</tr>
</tbody>
</table>

*The dissolved metal powders are diluted to 100 ml with 1% HCl. Then aliquots are diluted further to match the concentration range of Ni, Cr and Co in the air samples.
### APPENDIX C

**TABLE II**

Instrumental Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burner height</td>
<td>10 mm</td>
</tr>
<tr>
<td>Detector TP28 voltage</td>
<td>700 V</td>
</tr>
<tr>
<td>Hollow cathode lamp current</td>
<td>8 mA</td>
</tr>
<tr>
<td>Slit width</td>
<td>40 micrometers</td>
</tr>
<tr>
<td>Aspiration rate</td>
<td>4 ml/minute</td>
</tr>
<tr>
<td>Acetylene pressure</td>
<td>3.8 N/cm² (5.5 lb/in²)</td>
</tr>
<tr>
<td>Air pressure</td>
<td>3.4 N/cm² (5.0 lb/in²)</td>
</tr>
<tr>
<td>Scale-expansion</td>
<td>5X or 10X</td>
</tr>
<tr>
<td>Integration period</td>
<td>10 seconds</td>
</tr>
<tr>
<td>Wavelength</td>
<td>Ni 232.0 nm, Co 240.7 nm, Cr 257.9 nm (filter)</td>
</tr>
</tbody>
</table>
REFERENCES


Fig. 2. - Chromium calibration curve. (Channel B, interface filter.)

Acid medium: 1% HCl.
Fig. 3. Cobalt calibration curve at varying dilutions.

Acid medium: 1% HCl.
Fig. 4. Nickel, chromium and cobalt absorption at varying leaf currents.

Acid medium: 1% HCl
Fig. 6. Chromium absorption as a function of flame type and burner height.
Acid medium: 1% HCl
Fig. 7. Cobalt absorption as a function of flame type and burner height.
Acid medium: 7% HCl.
FIGURE 8 SCHEMATIC DIAGRAM OF LOW TEMPERATURE ASIFER