

MANUFACTURING CHEMISTS ASSOCIATION

1825 CONNECTICUT AVENUE, N W WASHINGTON, D C 20009 (202) 483-6126

October 9, 1974

RECEIVED

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To: Vinyl Chloride Research Coordinators

R. N. WHEATON, JR.

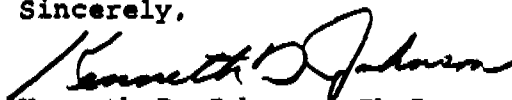
Subject: Proposal from Illinois Institute of Technology
Research Institute

Gentlemen:

Distributed herewith are copies of the subject proposal for research on the atmospheric chemistry of vinyl chloride. Please have your photochemistry consultant review this promptly. Your chairman has indicated his intention to call an early meeting of company representatives with particular competence in photochemistry to develop a final protocol and recommend a contractor to perform the necessary research.

Also enclosed is a copy of a report of some work done on vinyl chloride by a Shell affiliate and supplied by Dr. Maycock. He comments that this report has been submitted for publication and asks that proper credit be accorded it in any use of the contained data.

Sincerely,



Kenneth D. Johnson, Ph.D.

Secretary

Technical Task Group on

Vinyl Chloride Research

KDJ/mb

Enclosures:

IITRI Proposal

Photochemical Reactivity of Vinyl Chloride

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IITRI PROPOSAL NO. 75-68C

THE ROLE OF VINYL CHLORIDE IN THE URBAN-
INDUSTRIAL ENVIRONMENT

Secretary, Technical Task Group on
Vinyl Chloride Research
Manufacturing Chemists Association
1825 Connecticut Avenue, N.W.
Washington, D.C. 20009

Attention: Dr. Kenneth D. Johnson

Prepared by

Max Lustig
I.J. Solomon

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616

27 September, 1974

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IIT Research Institute
10 West 35 Street, Chicago, Illinois 60616
312 225-9630

September 27, 1974

Secretary, Technical Task Group on
Vinyl Chloride Research
Manufacturing Chemists Association
1825 Connecticut Avenue, N.W.
Washington, D.C. 20009

Attention: Dr. Kenneth D. Johnson

Subject: Proposal No. IITRI-75-68C
"The Role of Vinyl Chloride in
the Urban Industrial Environment"

Dear Dr. Johnson:

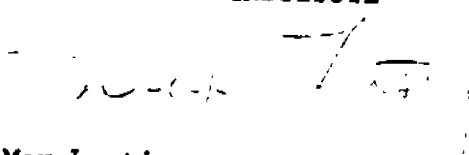
In response to your letter, dated August 6, 1974, IIT Research Institute is pleased to present a research program aimed toward the elucidation of possible health problems related to the presence of vinyl chloride in the atmosphere. The object of this proposed program is to find the answers as rapidly, facilely and thoroughly as possible, and each phase of the program will progress only if warranted from the results of the previous step.

A 6-man-month study is first presented with a cost estimate of \$35,000. This phase of the program is devoted to the gathering of information in the field regarding the concentration of vinyl chloride as well as species that may be formed from it in the ambient air surrounding several vinyl chloride plants. A careful search will be made for the presence of any harmful or even potentially harmful agents.

If the field testing shows the presence of undesirable intermediates and products and does not allow sufficient understanding of the processes leading to the formation of such substances, then a second phase of the program is suggested.

This phase is designed to obtain an understanding of the photo- and thermochemical behavior of vinyl chloride in the urban-industrial atmosphere. Based on the results of the first phase work, carefully selected laboratory scale and smog chamber experiments will be devised to achieve this goal. Kinetic information will be obtained on the decomposition of vinyl chloride as well as on the formation of its reaction products. The smog chamber research may also include the examination of the behavior of vinyl chloride in a typical Chicago aerosol. An accurate understanding of the chemical properties of vinyl chloride in polluted air is vital in order to establish appropriate counter-measures against the accumulation of vinyl chloride or toxic matter formed from its presence. The duration of this part of the program is estimated to be one-man-year if carried out to its entirety. No cost estimate will be given at this time.

Respectfully submitted,
IIT RESEARCH INSTITUTE


Max Lustig
Research Chemist
Chemical Energetics Research

I. J. Solomon
Chief Scientist
Chemistry Research

Approved by

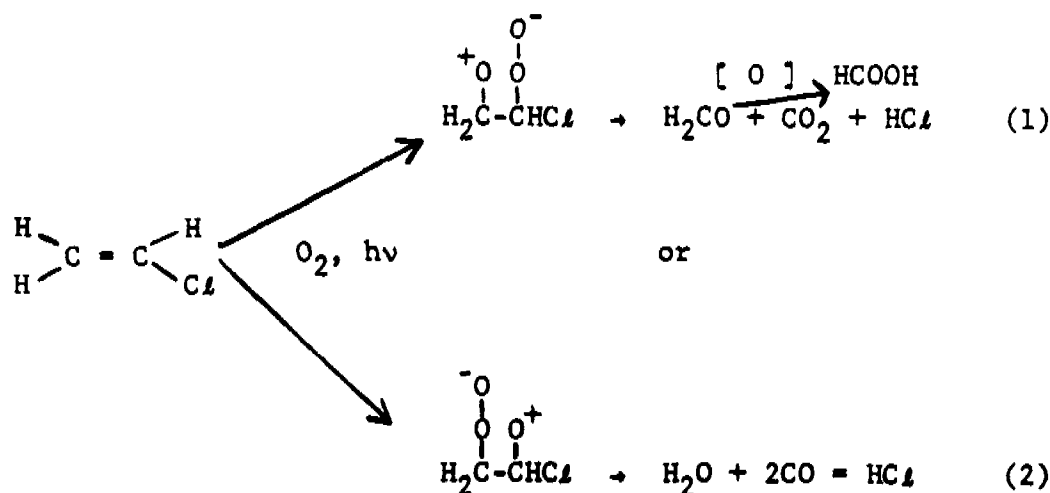
M. J. Klein
Director
Chemistry Research

THE ROLE OF VINYL CHLORIDE IN THE URBAN-INDUSTRIAL ENVIRONMENT

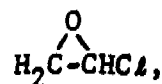
1. INTRODUCTION

The purpose of our proposed investigation is to ascertain the fate of vinyl chloride in urban-industrial air, particularly with respect to its toxic effect on human beings. The cause-effect relationship between vinyl chloride and cancer in workers, who are in daily contact with it, has recently become an important social issue. Possibly vinyl chloride may be a precursor to one or more carcinogens formed from it either in the atmosphere and/or in the human system. The important questions that must be answered are: (1) what happens to vinyl chloride once it enters the atmosphere, how long a time period does it remain intact, and (2) is it converted to potent carcinogens or otherwise hazardous substances or harmless agents.

Very little is known of its fate when it is present in the atmosphere other than its reported mild photoreactivity. However, Dr. P. Hanst¹ of the Environmental Protection Agency has performed smog chamber experiments and has found that vinyl chloride is photochemically converted to hydrogen chloride, water vapor, carbon monoxide, carbon dioxide, formaldehyde, and formic acid. The latter, formic acid, is a presumably an oxidation product of formaldehyde. These products can be explained, for the most part, as being derived via zwitter ion intermediates postulated by Criegee² from the ozonation of alkenes, i.e.,



According to Hanst¹, there is no evidence for the formation of an epoxide,



which has been postulated as a carcinogen. This epoxide may be formed by enzyme action on vinyl chloride when it is present in the human body, but confirmation of this point is not to be considered in the present work.

Because of Hanst's results, we propose proceeding directly to field tests as our first phase study and monitor for such constituents as vinyl chloride, hydrogen chloride, formaldehyde, formic acid etc. We will also perform a careful search for any air component that can be hazardous. If these results are not completely understood it may be necessary, with the agreement of IITRI and MCA, to conduct additional laboratory experiments.

2. WORK STATEMENT

2.1 Field Tests (Phase I)

- A large number of air samples will be collected and analyzed.
- Analytical techniques will be tested and developed to meet the program goals.

2.2 Laboratory and Smog Chamber Experiments (Phase II)

- If the objective of the program is not achieved by field testing, then, upon mutual agreement between MCA and IITRI, a variety of selected laboratory experiments will be conducted in order to determine the behavior of vinyl chloride towards known air pollutants.
- Analytical methods will be adapted to the continuous monitoring of the progress of the reactions.
- Reaction kinetics will be measured.
- These reactions will also be evaluated within a smog chamber.
- The smog chamber work will include the examination of the reactivity of vinyl chloride in a typical Chicago aerosol.

3. RATIONALE AND PROPOSED WORK

The results made available by Hanst¹ are very valuable because they provide us with the information needed to conduct field tests as our first stage of the program, since we know what substances for which to monitor. If, e.g., hydrogen chloride, formaldehyde etc. are present in greater than their normal atmospheric abundance and not produced from other sources than vinyl chloride plants, then these substances are the presumed products of this precursor, provided equations (1) and (2) are valid as being representative of the principal reaction paths. Conventional procedures for sampling and analysis should be adequate for this work, (see section 3.1.2). However, some effort would be required to determine the

stability and recovery of the vinyl chloride from the sampling collector. In addition, techniques already developed by IITRI for ambient air sampling and analysis will also be utilized in this program. We believe that the application of the gas chromatograph-mass spectrometer will be enormously beneficial to air constituent identification, for each of the numerous peaks expected on the gas chromatogram will be related to a mass spectral cracking pattern that can be used for identification purposes. Also available at IITRI is dual column chromatography which is one of the most refined techniques for resolving similar components in a mixture. If our analyses do not indicate the presence of known harmful agents or even potentially toxic substances, then the program can be re-evaluated at that time.

If, on the other hand, such substances are found, then it would be necessary to proceed to an in-depth examination to elucidate their nature and the processes leading to these materials with laboratory and smog chamber experimentation in order to conceive of procedures to retard their formation. Enough information needs to be accumulated in order to predict hazardous events in advance. To achieve this goal, information concerning the distribution of pollutants from a vinyl chloride facility, the chemical properties of these pollutants, plant production habit, and meteorological data must be correlated. Therefore, more samples need to be collected but under different weather or climate conditions and at various times relative to vinyl chloride production.

Consequently, the field testing will be conducted in the following manner. Initially, samples will be collected at three different plants, at the plant cite and at several instances from the plant simultaneously at various time intervals during the diurnal period. Approximately 30 samples will be collected at each plant vicinity. If unacceptable quantities of vinyl chloride or other hazardous substances

are identified, then the sampling will be performed once again toward the end of this phase of the program to check the initial results and also to take into consideration changes in weather or climatic conditions. Three plant sites will be selected to allow for the different nature of air pollutants in the environment of each plant. A portable weather station, developed by MRI, will be employed.

The laboratory and smog chamber experiments will be more time consuming and expensive and we will proceed to these studies only if it is felt (by agreement between IITRI and MCA) that the Field Monitoring Studies have not satisfactorily defined the problem and not answered the question as to the fate of vinyl chloride in the environment. Eventhough these studies may not be carried out, they will be discussed at the present time.

In the laboratory we plan to rapidly and as simply as possible demonstrate the gross chemical behavior of vinyl chloride individually or in combination with common air contaminants. For example, its thermo-(dark) and photochemical reactions with ozone, nitrogen oxides (NO_x) and various hydrocarbon derivatives including aldehydes etc. known to be present in the urban air will be studied on the laboratory scale using routine thermolysis and photolysis techniques. The information obtained from such experiments will permit kinetic and mechanistic interpretation of the reactions taking place. At the same time, techniques and methods for product identification and characterization will be developed. Particular scrutiny will be given to those agents which may be potential carcinogens or otherwise toxic. A number of analytical methods can be of general utility for detection and identification, such as gas chromatographic retention times gas chromatography-mass spectrometry combination, and several spectroscopic techniques (optical, nuclear magnetic resonance, electron paramagnetic resonance, mass spectroscopy), and wet

analytical procedures.

There can be differences between reactions taking place in the confines of a laboratory apparatus and those occurring in the open environment, i.e., in the former case surface contact can alter the course of reactions while in the latter the surface contact is minimized. Consequently, a simulation of the "open" environment can be obtained by use of a smog chamber. So the next step of Phase II will involve smog chamber studies of carefully selected reactions from the group considered above using vinyl chloride as the common substrate. Simulated sunlight will be applied. Analytical procedures will be adapted for the direct and continuous monitoring of products formed within the smog chamber, and comparisons will be made with the laboratory scale reactions.

Once the behavior of vinyl chloride is generally understood, more sophisticated experiments will be conducted involving vinyl chloride in a typical Chicago aerosol within the smog chamber; this aerosol will include not only molecular substances but also particulate and pollen matter. The same general analytical procedures will be applied to this phase of the research, except that the sensitivity of the techniques will be in the ppm and pphm range.

3.1 Field Monitoring Study

3.1.1 Field Sampling

Samples of air (between 90 and 180 samples) will be collected near three vinyl chloride facilities at various time intervals during the diurnal period and simultaneously at the plant cite and different distances from the plants. Samples will be analyzed at IITRI for vinyl chloride and other major components present. Those species which may be potentially harmful will be characterized by spectroscopic methods adapted to the determination of trace quantities. Sampling and

analytical techniques will be developed to satisfy the requirements of the program, although conventional procedures should generally apply. In addition several sampling methods developed at IITRI should be directly applicable to these studies, but, in this program as well as in others, preliminary sampling and recovery experiments will be required to determine the efficiency of the over-all method.

3.1.2 Analytical Methodology

Analytical procedures of high sensitivity for isolating and determining the organic and inorganic materials derived from vinyl chloride are well established. Some general methods also have been developed at IITRI for application to ventures similar to that proposed herein. All the procedures involve collection of gaseous substances by entrapment via absorption or adsorption in a matrix. The materials are then chemically or thermally desorbed and then measured by a technique using a two-column gas chromatograph coupled to a mass spectrometer or by chemical analysis. Furthermore, gaseous constituents in air can be identified in the ppm or even pphm range by a variety of spectroscopic techniques. Gas chromatograph-mass spectrometry is one very important tool that can be used for routine detection and identification at very low concentration levels. Optical spectra measurements (ultraviolet, visible, infrared) of ambient air can be obtained by placing gaseous samples either in cells containing mirrors to achieve long path lengths or by freezing the samples in a solid matrix at a low temperature. This analytical application has been used with success in other related studies. Some specific and relevant techniques already employed are described below.

3.1.2.1 Collection and Detection of Organic Vapors in Air

The organic components of air to be analyzed will be collected using method number P&CAM 127 developed by NIOHS. That is, organic vapors present in air are adsorbed on activated charcoal as a known column of air is drawn through the

specially designed tube. The compounds adsorbed on the charcoal are desorbed by carbon disulfide. A aliquat of the desorbed sample is then analyzed by gas chromatography. Vinyl chloride present in the mixture can be detected in the ppm level using a 6' x 1/8" stainless steel column packed with 0.4% carbowax 1500 on Carbopack A.³ The analyses are performed at room temperature and a nitrogen flow rate of 20 cc/min and its retention time is 2 min. If increased resolution is required due to sample complexity an alternate two column gas chromatographic technique developed at this institute can be used. The procedure involves the transfer of the substances producing an individual peak to a secondary column where additional separation can take place. The two columns are of opposite polarity for maximum separation.

3.1.2.2 Collection and Detection of Gaseous Hydrogen Chloride in Air

Gaseous hydrogen chloride may be detected in the air in the ppm level using a technique developed by T. Okita⁴. A known volume of air is drawn through a combination millipore-sodium carbonate impregnated filter. The chloride collected on the filter was entraced in boiling water. The analyses of chloride was made colorimetrically using the Volhard method. It is important to note that organic chlorides such as vinyl chloride are not trapped on the filter.

3.2 Laboratory and Smog Chamber Experiments

3.2.1 Laboratory Experiments

The results of Phase I may necessitate an extended program if hazardous agents are found. To obtain more elaborate statistics, more air samples will be collected under varying weather conditions and plant production schedules and the data will be correlated according to these variables. Based on the findings from the Phase I work, several selected photo- and thermochemical reactions between vinyl chloride and the known air pollutants, individually, will be studied. These experi-

ments would be the fastest and easiest manner to obtain results. The progress of the reactions will be monitored continuously. The products will be identified and the reaction kinetics will be measured.

3.2.2 Smog Chamber Extension of Laboratory Scale Experiments

Because gas phase reactions on a laboratory scale may be inhomogeneous due to surface effects, it may prove advisable to examine some of the same reactions in a smog chamber where these surface catalyzed effects are minimized. These reactions would also be followed by monitoring devices and kinetic comparisons will be made.

3.2.3 Urban Aerosol Smog Chamber Experiments

Because aerosols contain particulates in addition to molecular species, there may be differences between the chemistry of a real air and that simulated in the discussion above (see 3.2.1 and 3.2.2). Consequently, it may be desirable to extend our study if there are still inconsistencies between the field observations and those from experiments described above. For the "real" air a typical Chicago aerosol will be employed.

4. TIME AND COST ESTIMATE

The cost for the first 6-man-month Phase I work (field monitoring) is estimated to be \$35,000. This figure includes staff, labor, material and travel costs and will not be exceeded without your approval. Phase II cannot be costed at this time.

5. BACKGROUND

Of particular importance to this study is the current program which we are conducting for the U.S. Environmental Protection Agency in which we are characterizing PAN-Type compounds as well as their modes of formation and decompo-

sition in photochemical smog. This particular research was initiated by in-house funding and later supported by the NSF and presently by the EPA. A new program under consideration by the NSF deals with the isolation and identification of the illusive NO_3 radical, a short-lived substance proposed to be present in any atmosphere containing NO_x . Additional pertinent information detailing our experience is enclosed.

6. PERSONNEL CAPABILITIES, FACILITIES, AND INSTRUMENTATION

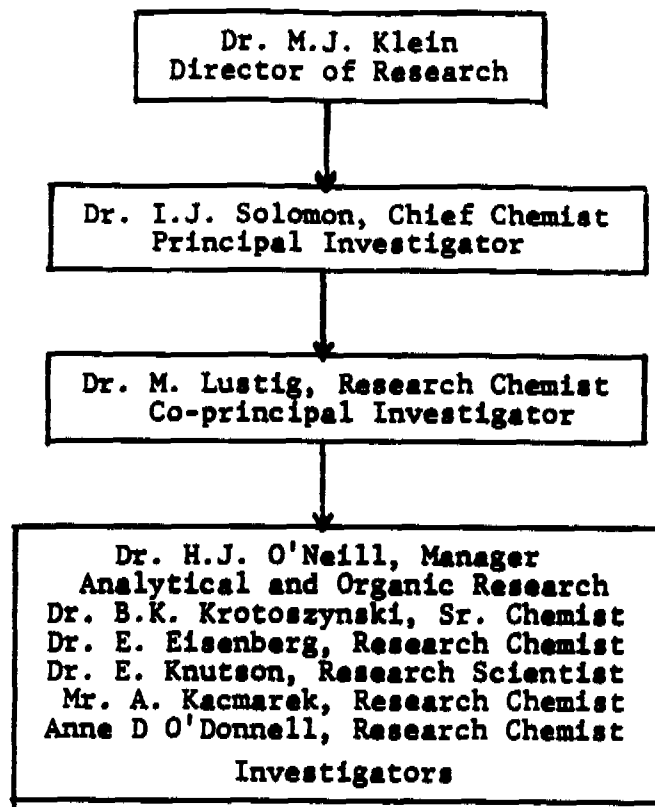
6.1 Personnel

The research personnel that will be associated with this program are eminently qualified to perform the intended research. Refer to personnel chart below. Dr. I.J. Solomon, Principal Investigator, has been managing environmental oriented programs for several years. Dr. M. Lustig, Co-principal Investigator, has been performing research on a current EPA air pollution project involving the study of the formation, decomposition and characterization of PAN-Type compounds formed in a photochemical smog. Dr. H.J. O'Neill will direct the analysis studies for this program. He has directed projects involving collection and analysis of ambient air samples. Dr. B.K. Krotozynski and Anne D. O'Donnell will be available for this project. These individuals are competent to perform the indicated analytical research. Mr. A. Kacmarek has conducted synthetic work on prior air pollution programs. Dr. W. Eisenberg is an organic photochemist whose background includes kinetic studies of primary photochemical processes, and Dr. E. Knutson is an Aerosol and Fine Particles Research Scientist and versed in smog chamber studies. More detailed information concerning these individuals may be found in the enclosures.

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Personnel Chart



6.2 Facilities

Important to this study are two aerosol chambers at IITRI, one of which would be dedicated for use as a smog chamber in the proposed study at no cost to the Manufacturing Chemists Association. Since the study of vinyl chloride reactions may involve toxic reaction products, safety of laboratory personnel is a consideration. This aerosol chamber was specifically designed for the study of toxic aerosols. Both the chamber and the laboratory in which it is housed are operated under negative pressure. The chamber can be vented through a high efficiency

particulate filter, with provision for a charcoal bed gas absorber.

For the proposed application to the study of vinyl chlorid reactions, the chamber will be equipped with a cylindrical gas reaction bag constructed of an appropriate polymer film. Ultraviolet (UV) irradiation will be accomplished by a battery of fluorescent "sun" lamps or "black" lamps mounted around the reaction bag. It is estimated that approximately 72 forty-watt lamps will provide the desired intensity.

The polymer film used to construct the gas reaction bag must be selected to have good UV transmission, good stability when exposed to UV and minimal surface chemical activity. Teflon is accepted as a lining material for smog chambers used in studies of photochemical smog reactions. Tests will be conducted to insure that Teflon does not emit halogenated hydrocarbon species which might interfere with the reactions of vinyl chloride.

Approximately 3 KW of electric power will be required for the UV lighting. It is anticipated that the massive steel construction and good thermal contact provided by the aerosol chamber in the photograph will prevent significant temperature rise in the volume of the chamber. The initial tests planned for the smog chamber will utilize air contaminated with high concentration of the common urban pollutants, as well as vinyl chloride.

Adequate laboratory space is available. Several photochemical apparatus for laboratory scale synthesis can be employed in this study. High vacuum facilities for the transfer and manipulation of gaseous substances are in routine service in the Chemistry Division of IITRI.

7. CONCLUSION

We have outlined a program intended to answer the pertinent questions regarding the behavior of vinyl chloride in polluted air. It is flexible and can be concluded at any stage depending on the results of the previous part and the requirements of the sponsor.

Bibliography

1. P. Hanst, private communication, unpublished results.
2. R. Criegee, Record Chem. Progr., 18, 111 (1957).
3. Sepelco, Inc. Bellefonte, Pennsylvania, 16823, Bulletin 44, 1974.
4. T. Okita, K. Kaneker, T. Yanaka and R. Sugai, Atmospheric Environment, 8, 927 (1974).

SYNOPSIS OF PAST IITRI PROGRAMS RELATED TO THE PROPOSED
VINYL CHLORIDE STUDY

Development of Analytical Methods and Test Equipment for
Determination of Hydrocarbon Contaminants, Contract No.
NAS8-2681

A monitor to continuously analyze the compressed gas supplies for non-condensable hydrocarbons, halocarbons and moisture at the 0.05 ppm level was developed and delivered.

Information Center for Organic Chemical Signatures, NSF,
Contract No. NSF-C514

The purpose of this program is to collect data to characterize the structure of organic compounds from which unknown compounds can be identified by matching signatures. Data from infrared, nuclear magnetic resonance, mass spectrometry and gas chromatography is being obtained and processed. The data is being indexed and prepared for computer (IBM 7094) input.

National Aeronautics and Space Administration (NASA) Technology
Utilization Survey on Air Pollution Monitoring Instrumentation,
NASA-Headquarters, Contract No. NASw-1716

Under this contract, Information Sciences Personnel conducted and published a technology survey on air pollution detection, monitoring, and control instrumentation, sensors, and techniques. Representatives of industry, academic and research institutions, as well as NASA were interviewed. The appropriate literature was searched to gather information on NASA-sponsored developments related to air pollution monitoring. Data was evaluated in terms of innovation to the state-of-the-art, and the dissemination of

Atmospheric Borane Monitor, Contract No. AF04(611)-7543

A small, portable instrument, sensitive to one part per hundred million, was developed. A small hydrogen-air flame was found to be a very efficient source for the excitation of the 2496 Å boron doublet.

Atmospheric Beryllium Monitor, Contract No. AF04(611)-7543

An instrument to monitor particulate beryllium oxide was designed and constructed. The sample is collected on continuous tape, such samples are irradiated with alpha particles, and the readout detected by a photomultiplier using scintillation counting techniques.

Continuous Analysis of Atmospheric Ozone, Contract No. AF19(604)-3884

A portable airborne analyzer was developed for detecting atmospheric ozone down to 0.1 ppm. The device uses the principle of catalytic decomposition of ozone which provides a thermal effect sensed by thermistors.

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