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Detection and Monitoring of Airborne Nuclear Waste Materials Annual Report to Department of Energy

J.R. MCDONALD, A.P. BARONAVSKI, L.R. PASTERNACK, V.M. DONNELLY, AND R.C. CLARK

Chemical Diagnostics Branch
Combustion and Fuels Branch
Chemistry Division

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The Chemistry Division of the Naval Research Laboratory in cooperation with the Department of Energy is carrying out research relating to detection, monitoring, and removal of several airborne species associated with nuclear facilities. Two of these projects relate to aerosol species. A series of new materials and formulations for manufacture of HEPA aerosol filters have been evaluated. A new fluorescence aerosol detection technique has been developed for challenging HEPA filter materials and installations. A new laser fluorescence Iodine-129 measurement technique has been

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developed for air monitoring. This detector has been perfected and a commerical prototype has been manufactured for field tests. An optical detection scheme for measurement of airborne tritium has been developed. Most of the components for this detector have been specified. A feasibility study was carried out to determine the potential for development of an optical diagnostic for measurement of airborne carbon-14. An optical detection scheme with an ultimate sensitivity of less than one part per trillion was specified. This instrumentation should be more economical than currently used techniques which have a detection limit of 100 parts per billion.

PREFACE

This annual report is prepared by Codes 6110 and 6180 of the Chemistry Division of the Naval Research Laboratory under contract with the Department of Energy Interagency Agreement No. EY-76-C-05-5057, Amendment No. A004. The research reported in this document covers tasks associated with the project "Detection and Monitoring of Airborne Nuclear Waste Materials". The research was conducted by J. R. McDonald, A. P. Baronavski, L. R. Pasternack, V. M. Donnelly, and R. C. Clark. Research involved in the other project included in this Interagency Agreement, "Development of Solid Adsorbants for Control of Nuclear Plant Off-Gas," (KZ-03-04-03) by V. R. Dietz and J. B. Romans is being reported in a separate document.

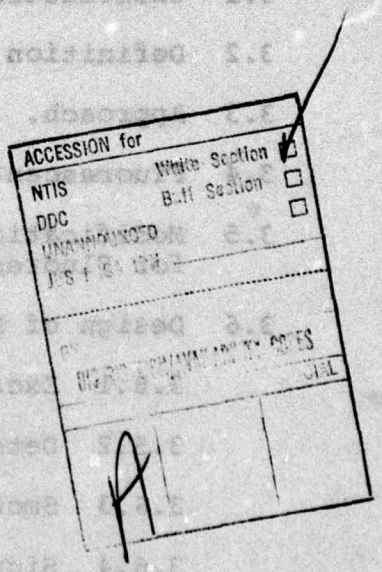


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SECTION I

1.0 INTRODUCTION

The handling, storage, use, and disposal of nuclear materials requires particular attention to the confinement of these species and prevention of their release to the environment within carefully defined limits. Of particular concern are the airborne nuclear materials, since they often occur in a highly diluted form in extremely large volumes of gas which make their monitoring and removal difficult. Under contract with DoE the NRL Chemistry Division has been carrying out research on various aspects of airborne nuclear materials.

Airborne nuclear materials fall into two broad categories: (a) gaseous species such as the atomic rare gases and molecular species such as iodine, iodides and tritium containing molecules and (b) particulate or aerosol materials which may contain any of the radio-nuclides. The concepts of filtration differ markedly for the two types of species. The monitoring and measurement of radio-nuclides has traditionally relied upon radio-counting techniques in which the physical form of the airborne material during measurement is not particularly important. With the advent of application of optical detection techniques to some of these materials, the molecular form of

Note: Manuscript submitted October 23, 1978.

the species must be given special attention. The range of projects underway at NRL under DoE contract covers filter materials and filter properties for both aerosol filters and adsorbents in gaseous filtration. In addition, new optical diagnostics are are being developed for application to aerosols and to gaseous materials such as iodine, organic iodides, tritium, and carbon dioxide.

This report is organized into individual stand-alone sections devoted to a report of progress in each of the materials evaluation and specie detection subtasks. It is intended that this report contain all pertinent information on each of the subtasks developed during this contract period. Portions of the information contained herein have been included in periodic interim reports of progress (made mainly as NRL letter reports) forwarded from NRL to DoE during FY-78.

SECTION II

A RADIOIODINE DETECTOR BASED ON LASER INDUCED FLUORESCENCE

2.1 INTRODUCTION

Of the six major iodine isotopes produced in nuclear reactors, ^{129}I represents only about 1% of the main fission product iodine isotope yield.[1] Although this isotope has the lowest specific activity and the lowest energy decay products, after a short period of cooling outside the reactor, the major iodine isotope present is ^{129}I. Because ^{129}I has a decay half-life of about 17 million years, new attention has been directed to its cumulative effects.[2,3] In spent fuel processing ^{129}I will have to be recovered and stored indefinitely because of its longevity. Because of the low specific activity, low energy decay products, and because ^{129}I is a minor iodine isotopic constituent in an active core, its detection by counting techniques is often slow and impractical.

Activated charcoal is the most widely used material employed for iodine removal, and it is also used as a means for decay storage. Because organic compounds of iodine are adsorbed less well than I_2 on activated charcoal substrates, in some applications charcoals are used which have been impregnated with substances which react chemically with I_2 and compounds of iodine or which undergo an isotopic

exchange.[1] Among examples currently used are charcoals impregnated with KI (or other iodine compounds) in which the stable iostope of the impregnant iodine can undergo an exchange (or reaction) with the radioiodine. Note that such an exchange can release a stable iodine into the effluent.[1] The efficiency of charcoal filters is strongly dependent upon their environmental history (particularly extended exposure to very high relative humidity)[4] and the desorption rate of iodine from the filters is strongly dependent upon temperature.[5] It appears that there exists a need to monitor and measure quantitatively in real time, iodine concentrations in several areas:

(a) as a continuous monitor to observe breakthrough behind critical filter facilities,

(b) as a monitor of fairly high ^{129}I ambient concentrations in spent fuel reprocessing, and

(c) as a monitor to observe accidental large releases of radioiodine in the spent fuel reprocessing cycle.

2.1.1 Proposed Research

For the reasons outlined above, in FY-77 NRL in cooperation with DoE contracted to design and laboratory test an instrument for the detection of low concentrations of $^{129}I_2$ in ambient atmospheres. The proposed instrument was based upon a laser induced fluorescence technique. In the design and evaluation of the proposed instrument the following

characteristics were stressed:

(a) the specified final instrument must be easily portable and capable of use under field conditions,

(b) the instrument should be specific for ^{129}I,

(c) the specified instrument should be capable of making real time measurements - preferably on flowing gas samples,

(d) the final field hardened instrument should be capable of continuous operation over extended periods of time, and

(e) the instrument should be as sensitive as possible consistent with a reasonable economic cost.

2.2 THE BREADBOARD DETECTOR

The successful breadboard detector is schematically outlined in Figure 1. The construction and evaluation of the detector is described in detail by Baronavski and McDonald in an earlier report.[6] The details of this report will not be reiterated here, however, a brief description of the pertinent design features will be reviewed. A $^{3}He^{22}Ne$ laser which emits at a wavelength preferentially adsorbed by $^{129}I_2$ is used as an excitation source. Absorption of the laser light raises an $^{129}I_2$ molecule to an electronically excited state. The electronically excited iodine molecule may be deactivated by collisions with other gaseous species or with the cell walls, or it may relax

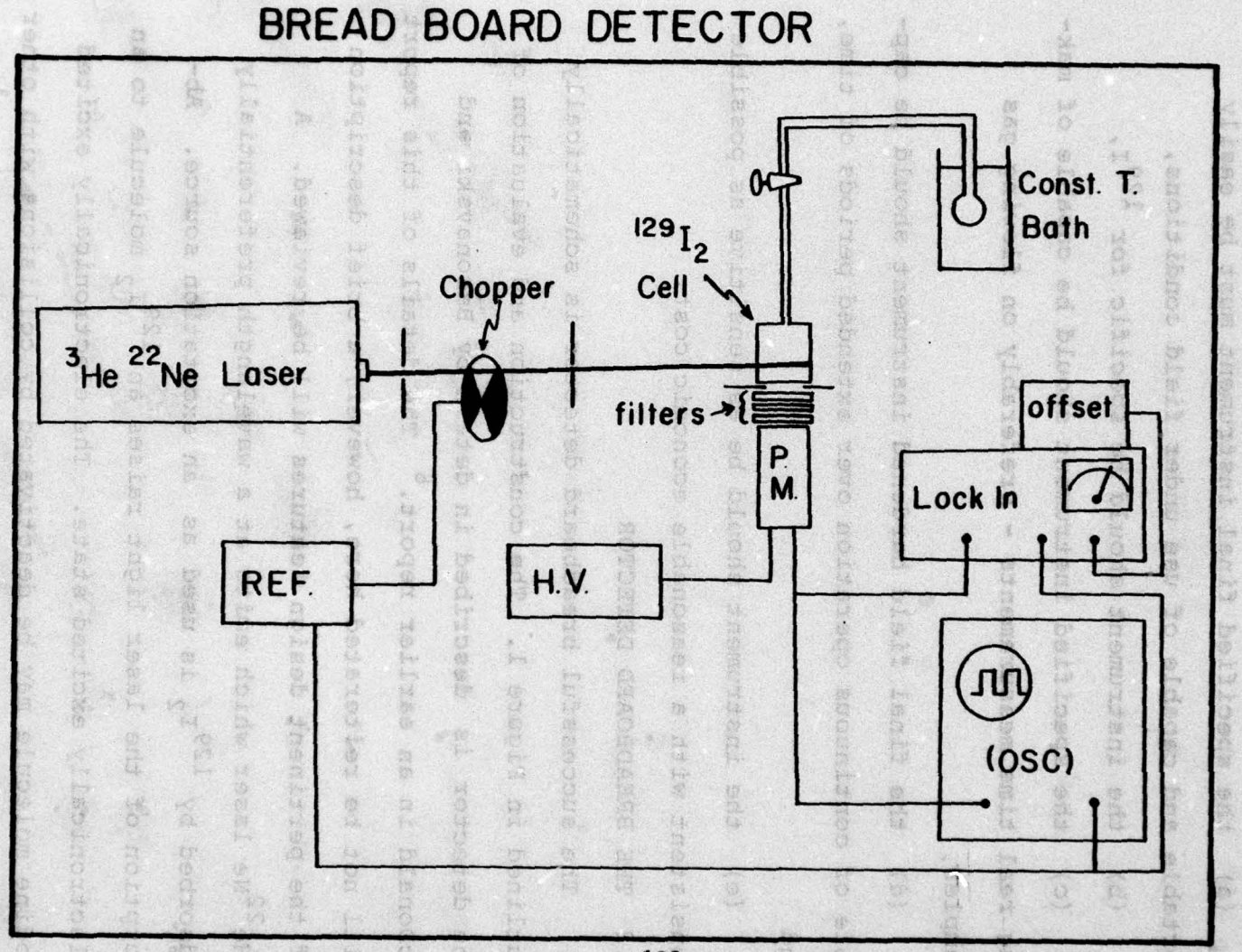


Fig. 1 - Schematic representation of $^{129}I_2$ laser fluorescence Detector

by emission of fluorescence at a wavelength longer than the excitation wavelength. This fluorescence emission is detected photoelectrically and processed electronically to provide a signal which is proportional to the concentration of the airborne radioiodine. Fluorescence detection curves for the detector with static cells are shown in Figure 2. The dashed portions of these curves represent signal levels which could be measured conveniently in our breadboard detection apparatus but which corresponded to iodine concentration levels that were too low to measure by independent techniques.

The discrimination of the breadboard detector against $^{127}I_2$ interference was measured to be greater than one hundred to one. This was considered to be adequate for most envisioned applications. The practical limit of sensitivity in atmospheric pressure samples was on the order of or better than 100 pgram $^{129}I_2/cm^3$. As this level of sensitivity and discrimination appeared to be within the limits required for application in spent fuel recovery operations, a decision was made to design, specify, and procure a field worthy prototype detector during FY-78.

2.3 THE PROTOTYPE MONITOR

2.3.1 Design Considerations

Various design concepts and criteria were considered for inclusion into the field prototype detector. It was decided that two independent detection paths should be

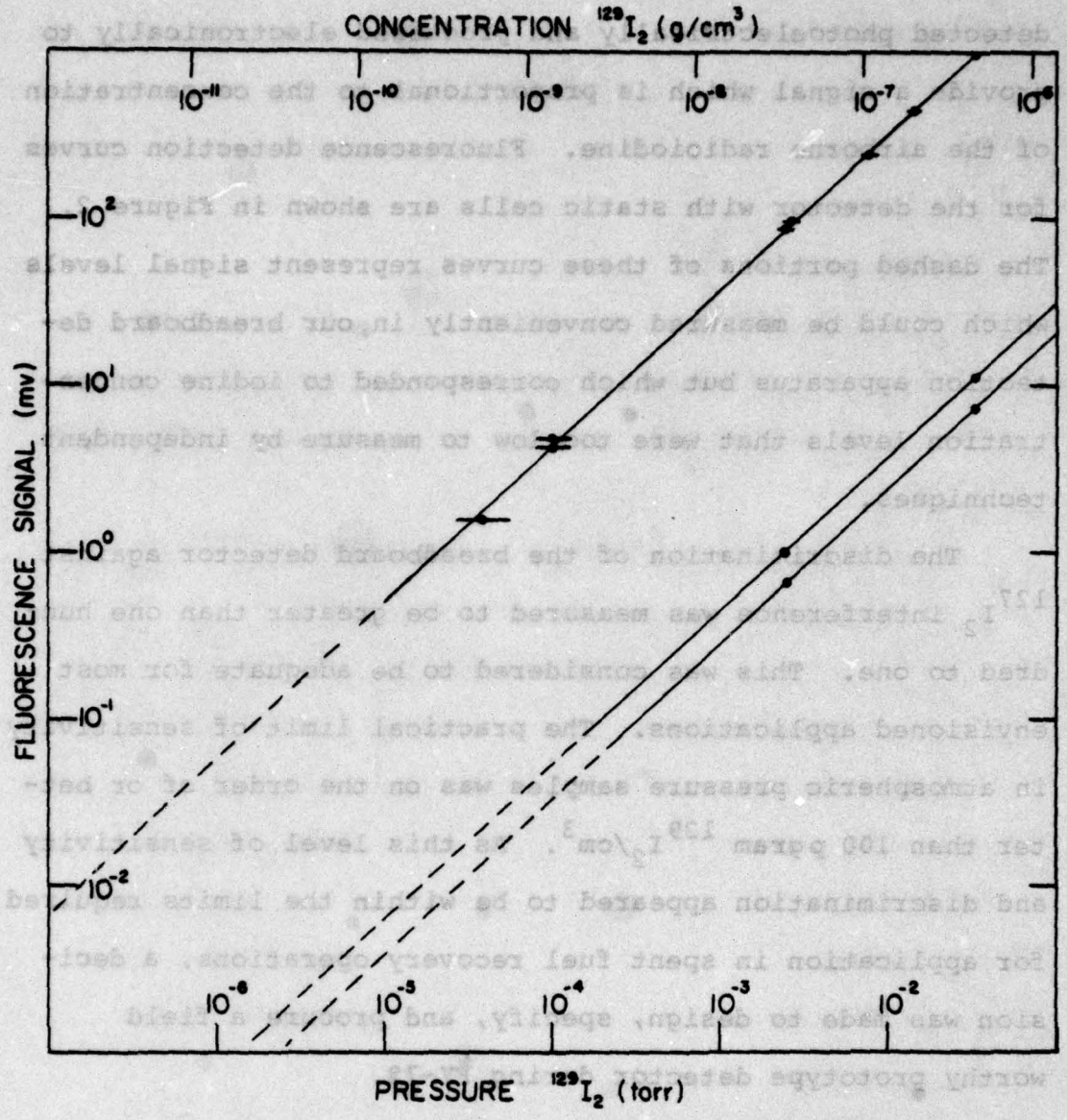


Fig. 2 - Working curves for $^{129}I_2$ fluorescence intensity as a function of pressure or concentration. The upper curve is measured for I_2 in evacuated static cells. The horizontal error bars represent the uncertainty in the I_2 pressure resulting from uncertainty in the absolute temperature-vapor pressure measurements for I_2. The vertical error bars are smaller than the size of the dots in the figure, i.e. $\sim\pm 10\,\mu$ volts. The center and lower curves are fluorescence signal response for $^{129}I_2$ in a static cell in the presence of 1 atm of argon and 1 atm of air, respectively.

included in the detector. The second cell would contain a sample of $^{129}I_2$. The fluorescence from this cell would be used to ratio against the unknown sample. In this manner, one could avoid the necessity of making real time absolute concentration measurements. In this way, changes in the laser output or optics would not effect the concentration measurements. Since appropriate facilities do not exist in the Chemistry Division at NRL to design and fabricate commercial level instrumentation, a decision was made to procure the prototype monitor via subcontract with the appropriate manufacturer.

Several potential vendors were contacted and informal meetings were held with each to discuss design and engineering feasibility for commercial construction of the desired detector. These discussions were centered about the major features to be incorporated into the prototype detector.

2.3.2 Procurement of Prototype Detector

Once it was determined that potential manufacturers were interested in providing the instrumentation, a procurement planning document was drawn up and published stating the design criteria and specifications for the commercial detector. Following are the salient features of these specifications.

DESCRIPTION/SPECIFICATION FOR MANUFACTURE OF PROTOTYPE $^{129}I_2$ MONITOR

Scope

Design, fabricate, test, and deliver a field portable prototype instrument to measure radioiodine concentrations in flowing airstreams.

Background

The Optical Diagnostics Section of the Chemistry Division, NRL, has been working under contract with DoE Oak Ridge operations office during FY-77 to investigate the feasibility of detecting airborne radioiodine $^{129}I_2$ at ambient concentrations in conjunction with spent nuclear fuel handling and processing.

A breadboard $^{129}I_2$ detector based upon a laser induced fluorescence technique was constructed and proved to have airborne sensitivity limits of $\leq 10^{-10}$ g/cm^3.

A preprint of an NRL Memorandum Report describing ther construction and evaluation of a laboratory model laser fluorescence instrument for $^{129}I_2$ detection is attached. The prototype instrument is to be based upon this breadboard design.

Specifications

An instrument shall be designed and fabricated based upon laser induced fluorescence to quantitatively measure concentrations of $^{129}I_2$ in flowing air or rare gas streams in real time and in an integration mode. The design shall

be based on the scheme in Figure 1 or an equivalent design which serves the same purpose.

The excitation device shall be a $^{3}He^{22}Ne$ laser, equivalent to the design and output characteristics of the Jodon Model HN-7 configured for TEM_{oo} operation.

The laser excitation frequencies will be specific for $^{129}I_2$ resonance absorption and not for other isotopes of iodine.

The excitation laser shall be modulated for signal processing purposes. The instrument shall be capable of automatic mode operation. Real time measurements and readouts should have automatic range switching and provision should be made to allow continuous use without operator assistance. In addition, an integration mode should be available to allow readout of total concentration over a period ranging from 1 second to 1 minute. All signal processing can be either analog or digital and is at the manufacturer's discretion, however, digital readout of concentrations is essential.

The instruments shall be capable of continuous operation over extended periods of time (5000 hrs.) without change of major components.

The instrument shall have a sensitivity of $\leq 10^{-10}$ g/cm^3 with a confidence level of 90% for a counting time of less than or equal to one minute. The instrument shall be

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capable of measurements over a dynamic range in excess of 10^5 in a direct readout mode.

Samples to be measured are to be ratioed against a sample cell containing a known concentration of $^{129}I_2$.

The instrument shall allow for internal reference measurements (i.e., laser power, absolute reference signal intensity, background signal nulling, etc.) to aid in field adjustment and trouble shooting.

The instrument shall be of ruggedized and modular design which shall allow for ease of portability and operation in the field. The only external connections required are a standard 110 volt ac power connection. As a guideline the weight of each instrument shall be no more than 60 lbs. and each instrument shall be no larger than 4' x 2' x 1'.

The fluorescence cells to be incorporated in the instrument shall be constructed of a good grade of silica or other non-fluorescing material. They shall be easily interchangeable and removable for cleaning.

Appropriate space allowance shall be made in each instrument for inclusion of a particulate filter in the air stream prior to the fluorescence cell.

The air stream prior to entering the fluorescence cell shall not come in contact with any metal surfaces. Quartz and/or Teflon are preferred air handling materials.

Provision shall be made for controlling and measuring the air flow through the fluorescence cell.

Provisions shall be made for separating the scattered He-Ne laser light from fluorescence of $^{129}I_2$ by appropriate combinations of dielectric and glass filters.

Provision shall be made by the contractor to interact with personnel at NRL in the laboratory evaluation of the detector and for field evaluation of the detector at DoE specified facilities. Two trips by the contractor, by NRL, and/or field facilities shall be required. Each trip shall require about three mandays at the field facility.

The instrument shall undergo preliminary tests and evaluation before delivery. It shall be tested to insure that it meets all the specifications. Such tests and evaluation data shall include but not be limited to the following:

a. Calibration curves for known amounts of $^{129}I_2$ demonstrating the specified sensitivity.

b. Tests and data to verify the specified dynamic range.

c. Demonstration of continuous operating capability for a minimum of 40 hours.

In addition to the above specifications, there are several other design features which the contractor should consider that would significantly improve the capabilities of

the instrument. The incorporation of these desired design features shall be considered a positive factor in the evaluation of the proposals.

a. Provision for a hot catalytic quartz pyrolyzer to convert organic iodides to molecular iodine is desirable. Pyrolizer shall be included immediately prior to introduction of gas stream into fluorescence detector.

b. Signal processing could be used to correct for isotopic scrambling of ^{129}I with ^{131}I and ambient ^{127}I since the decay rates of ^{129}I and ^{131}I are well known and their relative concentrations are a function of the history of the fuel in the reactor and the time which the fuel has decayed outside the reactor.

Concurrent with delivery of the instruments, the contractor shall deliver two copies of an Operator's Instruction and Maintenance Manual including electrical schematics and list of spare parts. Engineering drawings at Level 2, Production Prototype and Limited Production, shall be delivered with the instruments. These drawings must conform to MIL-D-1000A, Amendment 1, dated 20 February 1976.

Acceptance Tests:

a. Preliminary Acceptance - Within 120 days after effective date of contract (ADC), the contractor shall supply to NRL a test procedure to be used for final factory checkout and performance testing just prior to shipment of

equipment to NRL. This test procedure shall define all tests to be performed and list all instrumentation to be used in performance of tests. Comments as deemed necessary by the Scientific Officer will be documented and forwarded via Contracting Officer within ten working days. The contractor shall give NRL five days advance notice of the test such that the Scientific Officer may attend if he so elects. Copies of data generated as a result of the preliminary acceptance test will be furnished NRL at the time of equipment delivery.

b. Final Acceptance - Final acceptance of the equipment shall be at NRL after the equipment has successfully passed the preliminary acceptance specified above and has been installed and checked out.

Final Report - A final report shall be delivered at the time of equipment delivery. The final report shall include, as a minimum, the following: a report of any and all significant developments which occur or are discovered in the course of the design, fabrication, and testing phases of the contract.

After the normal competitive bidding procedure, the subcontract for fabrication of the detector was awarded to The Environmental and Process Instruments Division of The Bendix Corporation in Baltimore, Maryland. The instrument

was scheduled for delivery at the end of August 1978 and subsequently has been postponed for 30 days.

NRL has been working closely with the subcontractor to specify, where possible, appropriate design features in the instrumentation within the overall instrument procurement specifications. The following are instrumental features included which are not apparent from the procurement specifications.

a. Detection is by lockin amplifier. The chopper is a mechanical tuning fork which provides for an optimum chopping frequency with low space and weight requirements.

b. Photoelectric detection is by a pair of RCA 31000 photomultiplier tubes with two-inch photocathodes. This allows for maximum sensitivity and collection efficiency.

c. The signal processing and ratioing is automatic with automatic scaling and data presentation.

d. Physical space has been allocated for filters and a catalytic pyrolyzer, but these options have not been included.

Bendix has had problems in the fabrication and filling of the iodine reference cells for use in the instrument. After several failures it was agreed that the reference cells would be filled with $^{129}I_2$ by Bendix at the Chemistry Division at NRL making use of the ultra high vacuum

equipment in our Laboratory. These cells have now been filled satisfactorily.

Because of the delay in the delivery of the instrument, it is not possible to report the results of the quality assurance testing and sensitivity evaluation to be done by NRL in this report document. These evaluations will be carried out at the beginning of FY-79 and will be reported separately.

2.3.3 Prototype Evaluation and Modification

Several evaluations are planned for the prototype detector upon its arrival at NRL. The detector will be quality assurance tested under severe conditions anticipated in the field to determine any design or fabrication shortcomings and to assure its operation under continued use. In addition, several experiments will be conducted to determine absolute sensitivity, the possible problems from interferences, and to evaluate potential modifications.

It has been drawn to our attention that ambient concentrations of nitrogen oxides in the Idaho Falls effluents to be measured in the field evaluation are much higher than we anticipated. While theoretical considerations indicate that NO_2 at existing levels does not represent a serious interference, the importance of NO_2 in the iodine detector will be experimentally evaluated.

The sensitivity of the prototype instrument for the mixed isotope of molecular iodine $^{127}I^{129}I$ will be evaluated. Spectroscopic consideration indicates that the detector will be insensitive to the mixed isotope of iodine, but this must be measured (experimentally) with the prototype instrument to verify the supposition. These measurements will be carried out in static cells which are carefully prepared in our Laboratory.

Research at NRL during FY-79 has resulted in the development of a catalytic converter which quantitatively converts alkyl iodides to molecular iodine.[7] Since this instrument operates efficiently even at very low concentrations, and since it is relatively compact and inexpensive to construct, we will strongly consider modifying the detector to include the catalytic converter immediately prior to the gas inlet of the detector. A laboratory model of the convertor will be tested using labeled $CH_3{}^{129}I$ in airstream to evaluate its potential use and to determine the most appropriate design for inclusion in the prototype instrument.

2.3.4 Field Testing of Detector

Provisions have been made to field test the radioiodine detector at the Allied Chemical facilities in Idaho Falls. It is planned that the instrument will be ready for use in Idaho during the early part of FY-79. Plans for

this testing have been arranged with Dr. Robert Girton at the Allied facility. Personnel from NRL will accompany the detector to Idaho for the initial checkout procedure. After a period of testing at this facility the detector will be evaluated, appropriate modifications where required and feasible will be made, and final recommendations regarding its use will be formulated.

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SECTION III

FLUORESCENT AEROSOL DETECTOR FOR CHALLENGING HEPA FILTERS

3.1 INTRODUCTION

Extensive and stringent testing is required to achieve and maintain required performance levels for high-efficiency nuclear air cleaning systems. Such systems must achieve decontamination factors (DF) of at least 2000 (i.e., an efficiency of at least 99.5%) for aerosols having a number mean diameter (NMD) of less than 1 μm.[1] Testing of HEPA particulate filters is carried out with aerosols of dioctyl phthalate (DOP). In-place tests are made with polydispersed DOP of a mean light-scattering diameter of 0.7 μm, while quality control assurance tests are made with a monodisperse DOP aerosol of 0.3 μm. Typical equipment currently used for in-place DOP testing is the Naval Research Laboratory design linear readout forward light-scattering photometer. Because of the high efficiency of the filters to be tested, it is necessary to measure upstream concentration ranges of up to 10^5 times the threshold value.[2]

Because in-place filters may carry a relatively high particulate loading and because the in-place testing procedure may disturb the filters to be tested, it is often not feasible to determine whether the aerosol loading doped upstream from the filter facility is the same as

that exiting downstream.[3] It is desirable to determine downstream only those aerosols which were doped in upstream for testing purposes.

Significant further savings might be realized if two filters in series could be tested in place simultaneously. Such measurements would require a detector instrument dynamic range of $\gtrsim 10^8$ with significantly enhanced discrimination against nonfluorescent aerosols.

3.2 DEFINITION OF THE TASK

For these reasons NRL during FY-78 has undertaken research to develop a process for in-place testing of HEPA filters which will allow detection of only those aerosols loaded upstream to challenge the filter or filters. The following guidelines were set up for development of the desired instrumentation.

a. The test will employ real time measurement to provide instant evaluation of filters and to provide the capability to pinpoint leaks during testing.

b. The designed technique will conform as closely as possible to currently used practices specified by ANSI standards.

c. The specified measurement procedure must be routinely applicable and be capable of being carried out by nonspecialized personnel.

d. The testing procedure will not involve use of radio-nuclides or chemicals with severe toxicological effects. The test procedure will not adversely affect the subsequent use of the filter.

e. The economic cost of instrumentation must be maintained at a level commensurate with its widespread use in the field.

It was further understood that the development of test procedures for single filters and tandem filters in series represented significantly different levels of sophistication and sensitivity and that the costs of instrumentation for the two applications would likely be different. We have undertaken each of these tasks with the intention of developing techniques which should be applicable for either requirement.

3.3 APPROACH

The basic concept devised for the problem involves the use of fluorescent tagged aerosols which can be detected in the presence of relatively high concentrations of non-tagged aerosols and which will discriminate against the non-tagged particles. The test procedure developed is built around the following characteristics:

a. DOP aerosols are generated by currently used techniques.

b. The bulk DOP is doped with a scintillator which is automatically incorporated into the DOP aerosol.

c. The DOP aerosol, containing scintillator molecules, is to be measured by fluorescence techniques.

d. The technique to be developed must be capable of measuring total fluorescent aerosols simultaneously before and after the HEPA filter being challenged.

Three experimental approaches were envisioned as potential solutions to the fluorescent aerosol detection scheme. Each of these solutions requires a trade-off between dynamic sensitivity and design complexity and cost. To test single filters in place, a dynamic range of $\gtrsim 10^5$ is required with appropriate discrimination against non-fluorescent aerosols.

The testing of two filters in series requires an additional sensitivity increase of 10^3 with further enhancement in discrimination against non-tagged aerosols. A range of experimental approaches were investigated which should have application to each of these requirements. The experimental approaches investigated are as follows:

a. Use of fluorescent aerosols doped with scintillators which can be excited with a He-Ne laser at 632.8 nm and use of a modified light-scattering instrument to detect laser induced fluorescence from the aerosols. This technique would take advantage of the relatively inexpensive He-Ne

laser and currently available commercial light-scattering equipment. This approach appeared to offer the best trade-off between sensitivity and cost.

b. Use of fluorescent aerosols doped with scintillators which can be excited with a He-Cd laser at 442 nm and use of specifically designed fluorescence detection equipment to measure laser induced fluorescence of the aerosols. This technique would provide the ultimate in sensitivity and discrimination but requires more design complexity and moderate additional expense for the instrumentation.

c. Use of scintillator doped fluorescent aerosols to be excited with hot filament lamps or gas discharge arc lamps with use of modified light-scattering instruments or specially designed fluorescent detection equipment. This technique offers a low-cost alternative to the He-Cd laser technique with a concomitant small loss in sensitivity.

3.4 FLUORESCENT DYE SELECTION

The dyes to be used must meet several requirements:

a. The dye must have a suitable solubility in DOP.

b. The dye must have a high thermal stability and resistance to oxidation.

c. The dyes must have a high fluorescence quantum yield.

d. The dyes cannot be carcinogenic or toxic.

Since excitation with a He-Ne laser (approach number one) offered the best trade-off between sensitivity and cost, dyes which could be excited at 632.8 nm and fluoresce at wavelengths greater than 650 nm were investigated first. All major manufacturers and vendors of oil soluble dyes were investigated. While there are many potential candidates, no commercially available oil soluble dyes appeared to meet all the above requirements. Following this, an in-house screening was carried out on many further compounds not normally considered as commercial scintillators. The solubility restrictions ruled out most dyes currently used in the laser industry. One family of dyes was discovered which shows some promise - these are the metal phthalocyanine dyes. Their fluorescence quantum yields, as measured in our laboratory, are marginally acceptable, however, the Stokes shift in the fluorescence puts stringent requirements on the photomultiplier detectors. In addition, some of these dyes may pose toxicity problems. Because of the potential problems involved in the development of instrumentation around these dye systems, it was decided to investigate alternative number 3 (the use of classical light sources for fluorescent aerosol detection) and to make a choice at a later date based upon comparison of the two techniques.

Several fluorescent dyes and organic scintillator molecules were evaluated for solubility and fluorescence quantum efficiency for use with classical light source excitation. Fluoral-7GA was selected[4] because of its solubility in DOP and its high fluorescence quantum yield. A search of the literature disclosed no adverse toxicological data on the use of the chemical. The absorption and emission properties of fluoral-7GA are shown in Fig. 3. These properties are well suited for use with tungsten lamps and gas arc lamps.

3.5 MODIFICATION OF LIGHT-SCATTERING PHOTOMETERS FOR FLUORESCENCE DETECTION

Initial tests were performed to evaluate the potential for fluorescence detection with the forward light-scattering instrumentation currently used for in-place filter testing (for instance, the Phoenix Smoke and Dust Photometer JM-6000). The use of currently employed equipment would minimize the need to modify currently used techniques. The Phoenix instrument was modified for fluorescence detection in the forward direction by using optical filters to only pass light at wavelengths for fluoral absorption (Corning 7-59 filter) and to only detect light at wavelengths of fluoral fluorescence (Corning 3-69 and OCLI-cyan filters). Relative signal measurements were made with pure DOP smoke and DOP/fluoral smoke. No fluorescence could be detected

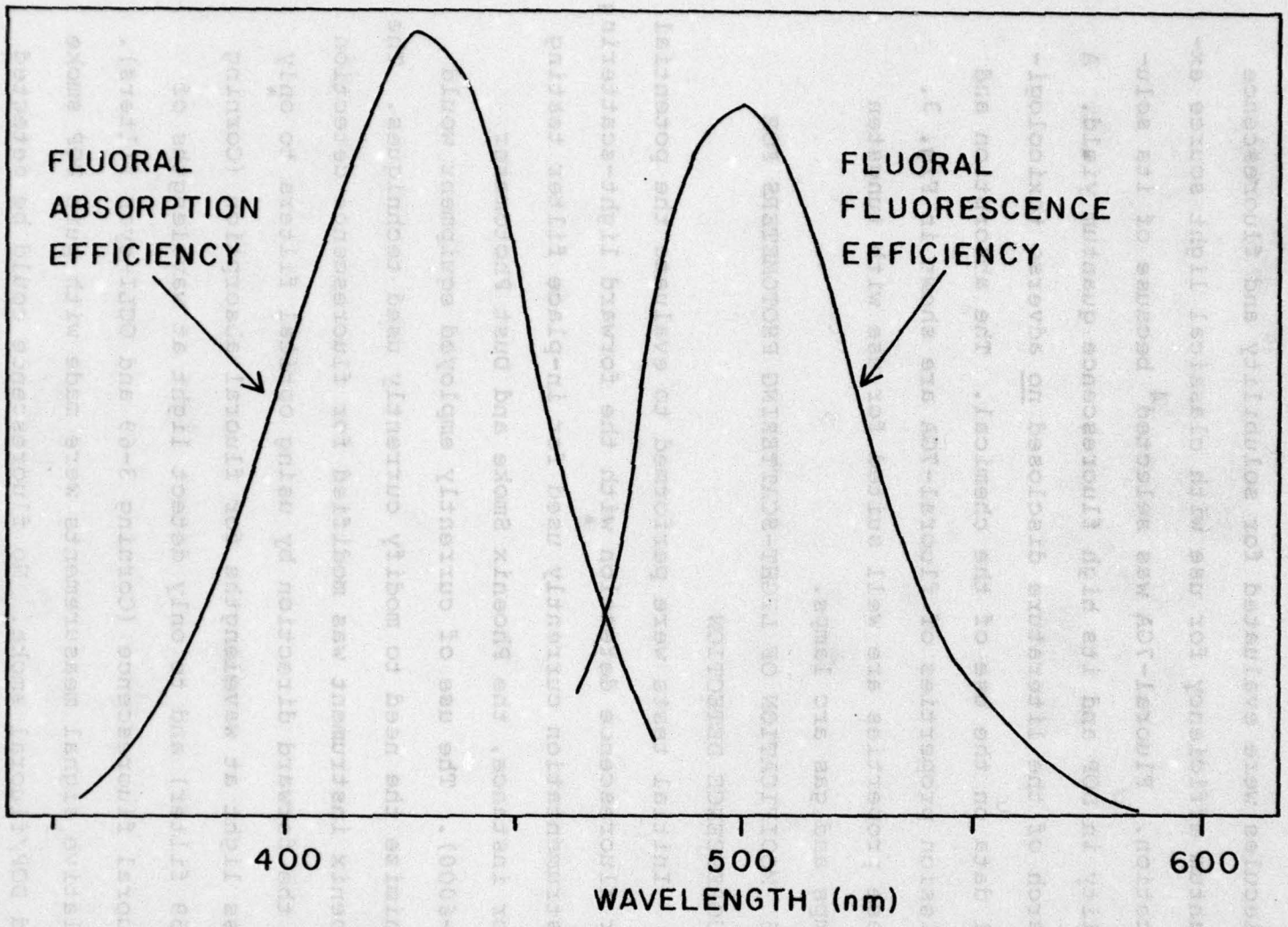


Fig. 3 - The absorption and fluorescence spectra of fluoral-7GA - DOP solutions.

within the limits of the noise of the scattered light measurements determined from the pure DOP smoke. It was determined that this instrument cannot successfully be further modified to detect fluorescence for the following reasons:

a. The light source is not adequate. Less than 10% of the visible light emitted by the light source (G. E. 1630 lamp) has a frequency in the fluoral absorption region. The lamps in these instruments represent twenty-five-year-old technological design.

b. The optical design of the light-scattering assembly is inappropriate for fluorescence detection. The design maximizes detection of forward light scatter which must be minimized for fluorescence detection. The assembly cannot be easily modified for 90° collection optics which is required for greater fluorescence signal/scattered light noise ratios.

3.6 DESIGN OF NEW AEROSOL SYSTEM

3.6.1 Excitation Source

It was decided to construct a fluorescence detector around a mercury lamp excitation source taking advantage of the 365, 405, and 436 nm Hg lines for fluorescence excitation. Three mercury excitation sources were evaluated:

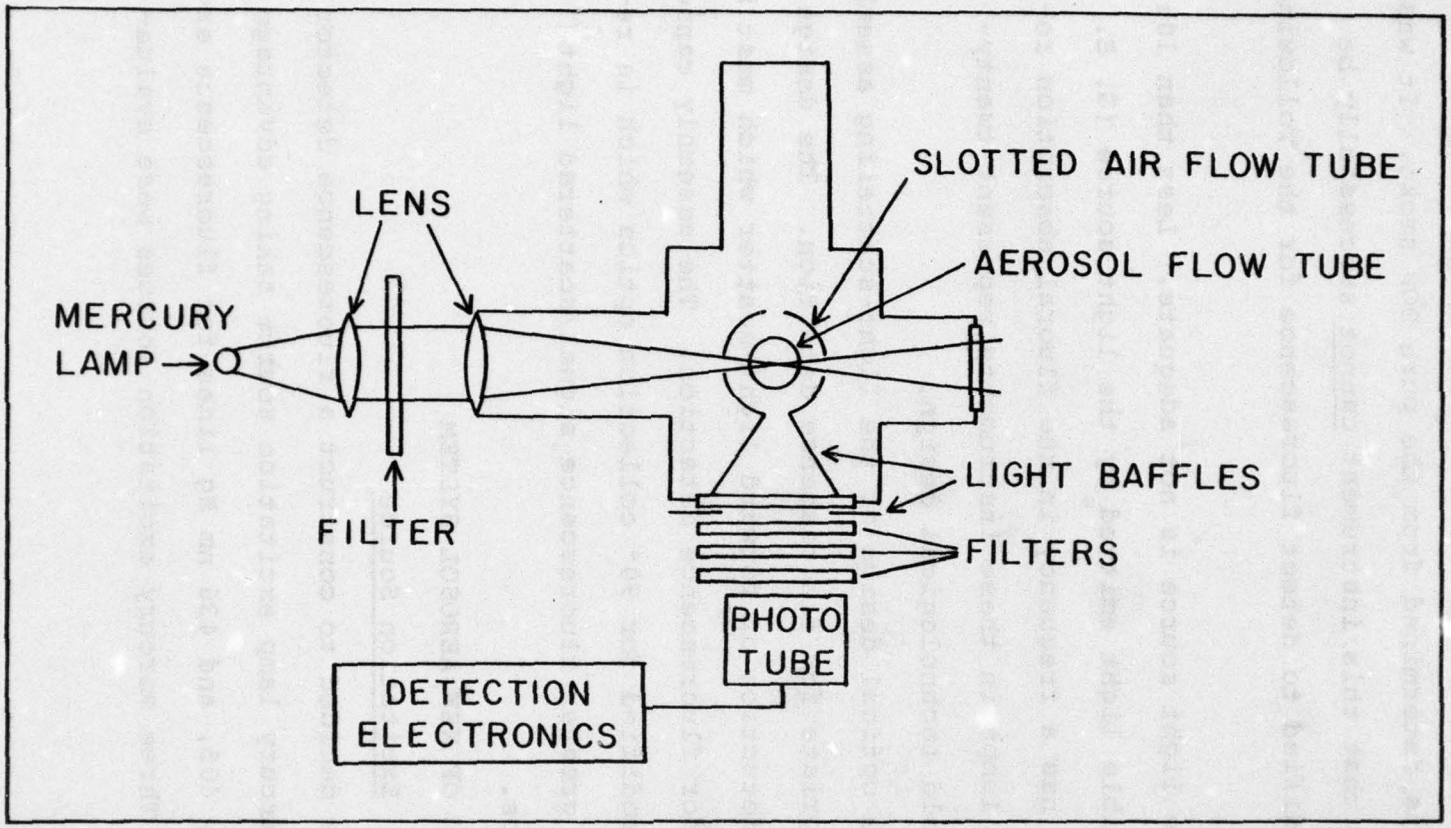


Fig. 4 - Schematic design of the fluorescence excitation and detection assembly used for fluorescent aerosol detection. The mercury lamp light is filtered to pass only fluoral excitation frequencies and focussed onto the aerosol stream. Fluorescence frequencies are isolated using appropriate glass and dielectric filters and collected at 90° using a 1P28 photomultiplier tube. Baffles are used to reduce scattered light, as shown.

a. A Gates 100 watt low-pressure mercury discharge source with the pyrex envelope removed,

b. a 1 K watt high-pressure arc source;[6] this lamp has an arc size of 5.9 x 3.0 mm, and

c. a 200 watt high-pressure arc lamp[7] with an arc size of 0.6 x 2.2 mm.

The evaluation of these lamp systems are given in the results section.

3.6.2 Detector Assembly

Because it is necessary to measure fluorescence signals at 90° to the excitation source, it was necessary to design and fabricate a new excitation and detector assembly. The design of this assembly is shown in Figure 4. The mercury light is filtered to pass the fluoral excitation frequencies at 312, 365, 405, and 436 nm (using a Corning 7-59 filter) and focussed onto the smoke stream in the coaxial flow system. Fluorescence is collected at 90° by an RCA 1P28 photomultiplier. Isolation filters (Corning 3-70 glass and Corion broad band 5000 dielectric) are used to pass only fluorescent light frequencies and to block the Hg lamp excitation frequencies. Light scattered from the walls of the chamber is blocked by the slotted tube and a conical light baffle, as shown in Figure 4.

3.6.3 Smoke Generator and Delivery System

The apparatus for smoke generation is the same as that currently used for in-place filter testing. The smoke delivery system is shown in Figure 5. This design maintains a well collimated aerosol smoke stream. We observe no buildup of background signal due to contamination of the system by fluorescent particles using this smoke delivery system.

3.6.4 Signal Measurement

The fluorescence from the excited scintillator molecules in the DOP aerosols is detected at 90° to the excitation beam in the photometer head as shown in Figure 4. The signal from the photomultiplier is quantitatively measured using either a picoammeter or a PAR HR-8 lockin amplifier. The lockin amplifier which is slaved to the 60 cycle arc lamp for the low-pressure Gates lamp and to an external chopper for the high-pressure arc lamp provides scatter and dark current suppression and signal averaging to enhance extraction of small signals from noise components.

3.7 EXPERIMENTAL RESULTS

3.7.1 From the 100 Watt Low-Pressure Mercury Discharge

Fluorescence signals were measured using the 1P28 phototube detector at 1000 volt power supply level. The output of the phototube, determined using the picoammeter and HR-8 lockin amplifier, are given in Table I.

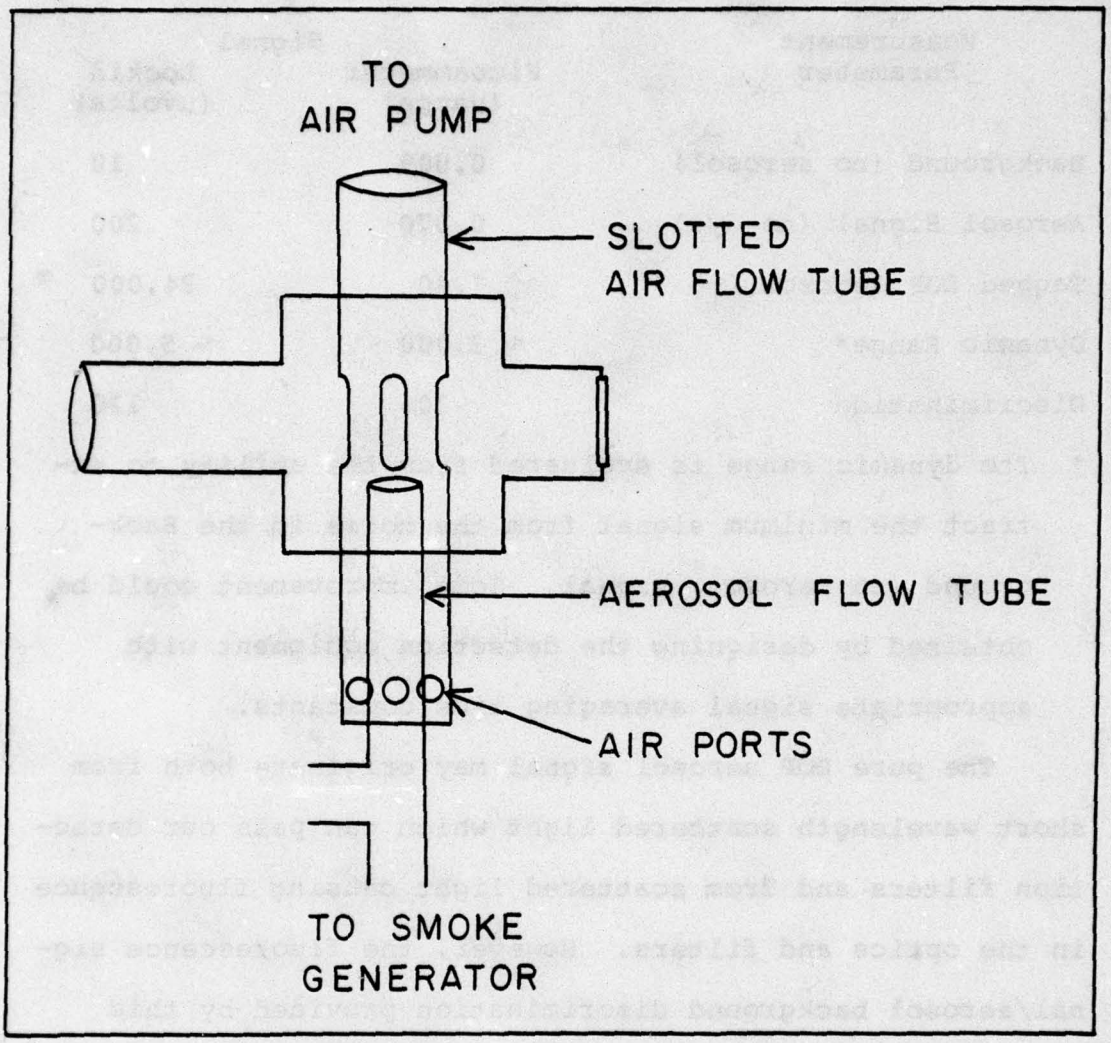


Fig. 5 - Schematic of the DOP aerosol delivery system. The aerosol smoke is collimated and contained by the coaxial airstream.

TABLE I

AEROSOL DETECTION WITH THE
100 WATT EXCITATION SOURCE

Measurement Parameter	Signal Picoammeter (μamps)	Signal Lockin (μvolts)
Background (no aerosol)	0.009	10
Aerosol Signal (no dye)	0.070	200
Tagged DOP Aerosol	7.40	24,000
Dynamic Range*	∿ 3,000	∿ 5,000
Discrimination	106	120

* The dynamic range is evaluated from the ability to extract the minimum signal from the noise in the Background (no aerosol) signal. Some improvement could be obtained by designing the detection equipment with appropriate signal averaging time constants.

The pure DOP aerosol signal may originate both from short wavelength scattered light which can pass our detection filters and from scattered light causing fluorescence in the optics and filters. However, the fluorescence signal/aerosol background discrimination provided by this technique is greater than a factor of 100. The sensitivity obtained using the low-pressure arc lamp falls just short of the 10^5 dynamic range which is required for testing single HEPA filters.

3.7.2 From the 1,000 Watt High-Pressure Mercury Arc Lamp

Typically, signals were generated using the 1 kwatt high-pressure arc operating at 500 watts and measured at 925 volts on the 1P28 photomultiplier. The large arc of this lamp is not ideally designed for use with the photometer head. Reducing the output of the lamp stabilzes the arc and reduces scatter from the very hot envelope of the lamp. Typical results using this excitation system are shown in Table II.

TABLE II

AEROSOL DETECTION WITH THE

1,000 WATT MERCURY ARC LAMP

Measurement Parameter	Signal Using Picoammeter
Background (no aerosol)	0.055 μamp
Aerosol Signal (no dye)	4.25 μamp
Tagged DOP Aerosol	290. μamp
Dynamic Range	$\gtrsim$ 200,000
Discrimination	68

The use of the high-pressure arc source over the low-pressure diffuse source gives a factor of ~40 improvement in the sensitivity of the instrument. With the use of lockin detection, one could easily achieve a 10^6 dynamic range operating in this mode. However, the discrimination using the high-pressure arc source is reduced to about 70:1.

3.7.3 200 Watt High-Pressure Compact Arc Lamp

The experiments with the low-pressure diffuse source and the 1 kwatt high-pressure arc lamp have allowed us to specify the optimum excitation system for the detector. For this purpose a high-pressure 200 watt compact mercury arc source has been ordered. The very small arc in this lamp, 0.6 x 2.2 mm, will behave essentially as a point source and is ideally suited to our photometer head. The power delivered to the aerosol stream should be greater than that of the kilowatt source and because of its dimensions the scattered light discrimination against nonfluorescent aerosols should be 100-300.

3.8 EVALUATION

3.8.1 Applications and Limits of Sensitivity

During this fiscal year our Laboratory studies have centered around designs employing classical light sources for fluorescent aerosol detection. Our Laboratory experiments clearly demonstrate that the fluorescent aerosol detection technique can be used to challenge in-place single HEPA filters. It seems unlikely that this technique with the use of arc lamps can produce the sensitivity required to challenge HEPA filters in series. (See Section 3.8.3 below.) However, the fluorescent aerosol detector with mercury arc lamps is superior to the currently used forward light scattering photometers because it has an equivalent

dynamic range and discriminates against nonfluorescent aerosols. In addition, laboratory experiments lead us to believe that the use of these fluorescent aerosols should make it possible to locate visually the origin of filter leaks. Illumination of filters from the downstream side with hand held uv lamps should create a yellow-green fluorescence at the point of a leak after the aerosol tests.

3.8.2 Prototype Fluorescent Aerosol Detector Using Classical Light Source

We recommend that DoE consider the above-described detector as a replacement for the currently used light-scattering detectors. This detector will be self-contained, readily portable for field use and similar in operation to the currently used aerosol detectors. The proposed instrument when commercialized should have a cost similar to the current light-scattering photometers and will be usable with the current smoke generators used for in-place testing.

This evaluation can best be made by production of a field worthy prototype instrument which can be evaluated in the field at specified facilities. We anticipate that such a prototype could be obtained and tested with appropriate support during FY-79.

3.8.3 Testing of HEPA filters in Series

The fluorescent aerosol detector which we have developed during FY-78 which uses mercury lamp excitation does

not have the dynamic sensitivity required for testing series filters. We have concentrated on this design because the widespread use of such detectors requires that cost and simplicity be maintained at the lowest level possible.

However, the fluorescence technique which we have developed can be extended to provide several orders of magnitude greater dynamic range of sensitivity by replacing the mercury arc with a He-Cd laser (λ = 442 nm). The laser can be incorporated into our current breadboard fluorescent aerosol detection equipment. The cost of the laser source is ~$4,000, as compared to ~$1,000 for the mercury arc source and associated power supply. We anticipate that the sensitivity and dynamic range of the fluorescent aerosol detector with He-Cd laser excitation should be easily adequate for in-place testing of two HEPA filters in series.

We recommend that the investigation of the fluorescent aerosol detector using He-Cd laser excitation should be made in FY-79.

3.9 REFERENCES

1. "Nuclear Air Cleaning Handbook"
C. A. Burchsted, J. E. Kahn, and A. B. Fuller
ORNL/ERDA 76-21.

2. "Design, Construction and Testing of High Efficiency Air Filtration Systems for Nuclear Application" ORNL-NSIC-65 (1970).
3. "In-Situ Testing of Tandem HEPA Filter Installations with a Laser Single Particle Spectrometer System" B. G. Schuster and D. J. Osetek 15th DoE Nuclear Air Cleaning Conference, Boston, Mass. Aug 78. Note, in particular, problems resulting from the CMR-2 filter tests.
4. Exciton Chemical Company, Dayton, Ohio
5. George W. Gates and Company, Long Island, N.Y.
6. Hanovia Model 941B-1 Electro Powerpacs Corporation, Cambridge, Mass. 02139.
7. Osram Model HBO 200W/2, Electro Powerpacs Corporation, Cambridge, Mass. 02139.

SECTION IV

AN OPTICAL DETECTOR FOR TRITIUM

4.1 INTRODUCTION

Tritium is produced by numerous mechanisms associated with various operational components of nuclear reactors. Its production is indigenous to these operations and represents an increasing problem both to the nuclear industry and in fuel handling and reprocessing operations. Chemically the isotope exists in the gas phase primarily as HTO and HT with some contribution from tritiated hydrocarbons. The relative importance of these species depends on the production and handling environment of the isotope.

The maximum permissible concentration of tritium in air in the chemical form of HTO is 2×10^{-7} $\mu C/cm^3$. However, because the radioactive decay is weak (β = 18 Kev), it is one of the most difficult nuclides to measure in real time.[1] Recently, Fernandez and Girton[2] have evaluated currently existing tritium analysis techniques and made recommendations for further development.

4.1.1 Detection Techniques

Currently existing detection methods make use of various radio-counting techniques such as ionization chambers,[3,4] liquid scintillation[5,6] counting, solid scintillators,[1] and proportional counters.[7,8] Each of these detection techniques suffer from unique limitations, however,

they have in common a potential interference problem from other nuclides such as ^{85}Kr and ^{14}C. In addition, a sensitivity to gamma radiation poses a problem in detection.

Because of the interference problems and because the tritium exists in a variety of molecular forms, detection schemes must make use of catalytic converters to produce a single molecular isotope and separators to remove the tritium from large volumes of air containing the interfering nuclides.[2] The separators typically make use of either silica gel or molecular sieves for trapping of the aqueous component. This operation reduces the detector to operating in a non-real time batch mode. The most novel separator under investigation makes use of a technique referred to as permeation distillation.[2,9,10] In this application the tritiated water is continuously removed from the airstream in a gaseous counter current extraction. This technique is amenable to continuous monitoring applications and gives an adequate separation from ^{85}Kr and high levels of NO_2.

Under contract with DoE in FY-78 we have undertaken a project to develop an alternative type of tritium detector. An optical detection scheme based upon resonance emission from tritium atoms holds promise of providing an analytical technique which is independent of the problems of radiocounting in the presence of other nuclides and gamma radiation fields.

4.2 DEFINITION OF TASK

The objective of this project is design and demonstrate an optical detection scheme for measurement of tritium concentrations in air at a level suitable for use as a monitor in the industry. The guidelines for such a detector to be competitive with radio-counting schemes are given below:

a. Sensitivity must be better than $\sim 5 \times 10^6$ $^3H/cm^3$ in air which corresponds to the MPC for HTO.

b. Real time or near real time measurement is necessary.

c. The device should be free of interferences from airborne species present in the airstream.

d. The device must be simple to operate and capable of continuous long-term service.

e. The device must be economically competitively with radio-counting instrumentation capable of the same operational sensitivity.

4.3 DESIGN OF THE OPTICAL DETECTOR

4.3.1 Spectroscopic Considerations

Spectroscopically, hydrogen is the simplest of all atomic systems. However, absorption measurements are extremely difficult since the lowest lying ground state transition is the $2p \leftarrow 1s$ (Lyman α line) at 121.6 nm in the vacuum ultraviolet. A diagnostic tool based upon this resonance would be complex and prohibitively expensive. Emission measurements, on the other hand, have been carried

out by several workers[11-16] on the so-called Balmer Series (involving hydrogen atom transitions from high lying states terminating on the n = 2 level). These emission lines begin in the visible and extend through the ultraviolet region of the spectrum.

Therefore, it would be advantageous to devise a method by which concentrations of T atoms may be found relative to H atom concentrations in real time utilizing the Balmer line at 656.3 nm. The reasons for the choice of this spectroscopic feature are:

a. the Balmer α line is the most well studied of this series; the hyperfine structure is understood and well documented[17,18] for H, D, and T atoms,

b. the wavelength is convient for use with photomultiplier detectors having gain in excess of 10^7 and which can take advantage of the extremely high sensitivity for photon counting purposes,

c. the Balmer α line is the most intense line of the series, and

d. the spectroscopic isotope shifts are conveniently large; for example, (ignoring hyperfine structure for the moment) the $3D_{5/2} - 2P_{3/2}$ transition occurs at 15233.07 cm^{-1} (656.278 nm), 15237.215 cm^{-1} (656.099 nm), and 15238.594 (656.040 nm) for H, D., and T. atoms, respectively. The isotope splittings relative to hydrogen are therefore 4.145 cm^{-1} for Deuterium and 5.524 cm^{-1} for Tritium.

To this point the hyperfine structure in the Balmer series has been ignored. For each atom the Balmer α line is composed of several hyperfine components. All these spectroscopic features are well understood. Table III gives a listing of the allowed transitions for H_α, D_α, and T_α, and Figure 6 shows a stick diagram of the spectral features of interest. It is easily seen that all lines of a given isotope are grouped within $\sim$0.5 cm^{-1} and that a spectral overlap of H, D, and T isotopes does not pose an interference problem. What really concerns us, then is the minimum separation between D_α and T_α; this is given by 15238.460 - 15237.544 = .916 cm^{-1}. The minimum resolution required to spectroscopically separate D_α lines and T_α lines is $\sim$0.9 cm^{-1}. In this spectral region, monochromators can easily achieve this resolution but must be of long path length and, consequently, low light gathering power. In addition, they are large and expensive. For this reason, a moderately high resolution Fabry-Perot Etalon Spectrometer should be used.

4.3.2 The Breadboard Detector

Conceptually, the breadboard tritium detector is approached from a building block point of view. The basic concept for the detector is schematically outlined in Figure 7. We visualize four major components in the detector.

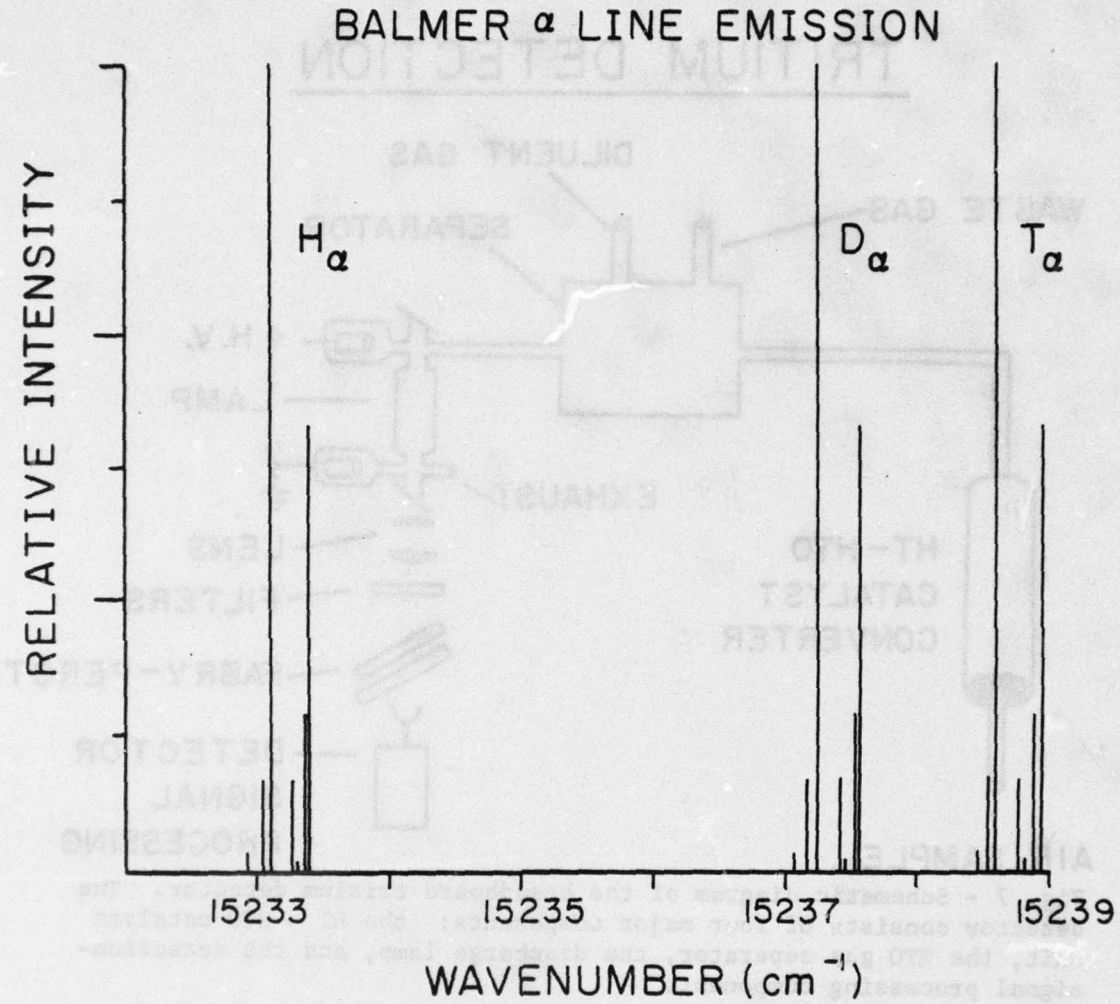


Fig. 6 - A spectroscopic stick diagram showing the Balmer α emission of H atoms near 15,233 cm^{-1}, D atoms near 15,237 cm^{-1}, and T atoms near 15,239 cm^{-1}. Each "atomic Line" is composed of several hyperfine components, as shown.

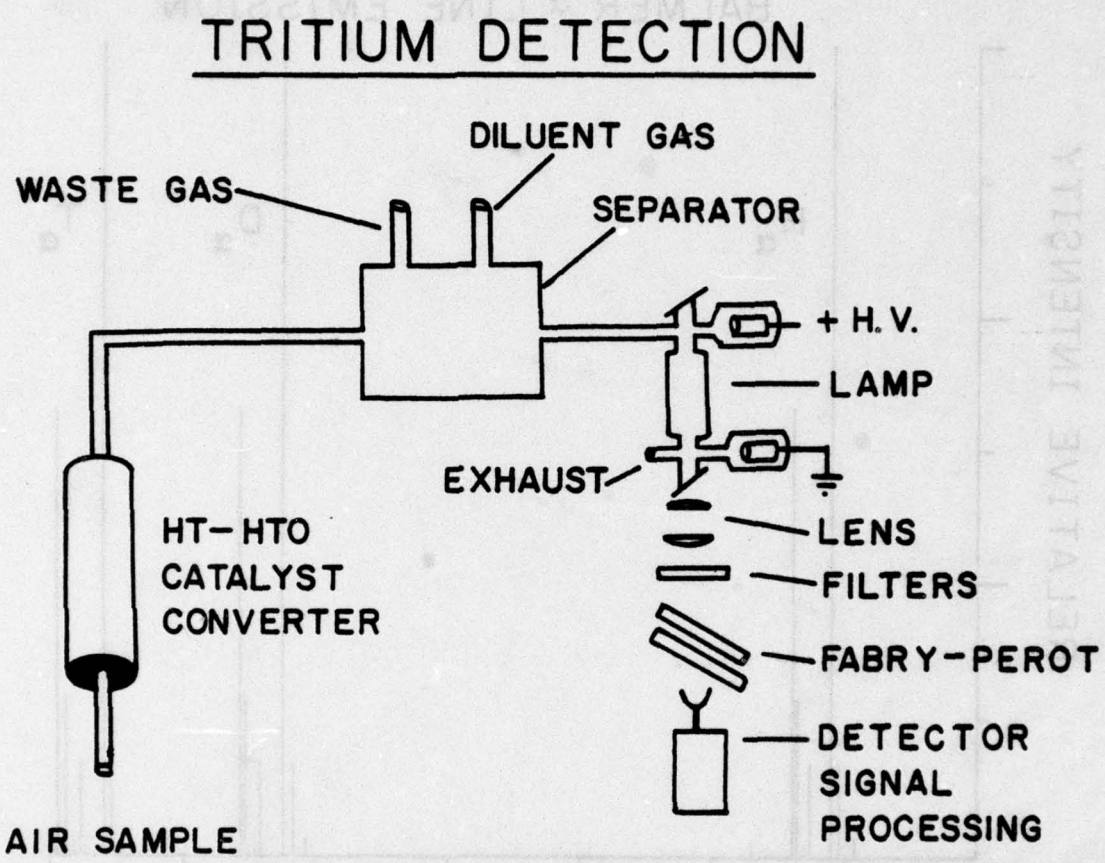


Fig. 7 - Schematic diagram of the breadboard tritium detector. The detector consists of four major components: the HT → HTO catalyst unit, the HTO gas separator, the discharge lamp, and the detection-signal processing component.

TABLE III

SPECTROSCOPIC VALUES FOR THE BALMER TRANSITION OF ISOTOPIC HYDROGEN SPECIES α

Transition	Wavenumber of Line (cm^{-1})			Relative Line Strength
	H_α [a]	D_α [a]	T_α [b]	
$3S_{1/2} - 2P_{3/2}$	15232.936	15237.081	15238.460	25/128
$3D_{3/2} - 2P_{3/2}$	15233.033	15237.178	15238.558	1
$3D_{5/2} - 2P_{3/2}$	15233.070	15237.215	15238.594	9
$3P_{1/2} - 2S_{1/2}$	15233.256	15237.401	15235.779	25/24
$3S_{1/2} - 2P_{1/2}$	15233.302	15237.447	15238.825	25/256
$3P_{3/2} - 2S_{1/2}$	15233.364	15237.509	15238.888	25/12
$3D_{3/2} - 2P_{1/2}$	15233.399	15237.544	15238.923	5

a) From reference 17.

b) From reference 18.

4.3.2.1 Converter

Since the tritium effluent occurs in the form of HT, HTO, and a minor amount of tritiated organics, the likely first step will be to convert these to a single molecular species, HTO. Given the fact that one need not absolutely convert all tritium bearing species to HTO, this catalyst system can be very modest. A conversion efficiency of >98% can be attained for minimum economic investment in a unit which will not make severe physical space demands. One can tolerate a less than absolute 100% conversion since an uncertainty in conversion efficiency to HTO of ∿2% will have a vanishingly small effect on the precision of the final tritium concentration measurements.

4.3.2.2 Separator

The present design concept provides for a separation stage to strip the aqueous tritium containing phase from the remainder of the bulk airstream. It is not absolutely certain at the time that a separation stage will be required. However, provision is being made for its inclusion on the assumption that it will be needed. Both batch type separators and continuous separators are being considered. For batch type separators both molecular sieve beds and cryogenic trapping are possible techniques which can be used. The sieve traps reviewed by Fernandez and Girton[2] and cryogenic trapping will each trap CO_2 and NO_2 in addition to HTO. While this makes these separators unsatisfactory for radio-counting detection, these polar species should not pose an interference problem with the optical detection scheme.

The use of a continuous separator is more appealing since it would allow a real time capability for tritium monitoring. The permeation distillation driers manufactured by Perma Pure Products[10] and used by Girton[2,9] show promise for use in separating the aqueous components from the bulk airstream. These driers are to be evaluated for this purpose during this research.

4.3.2.3 Discharge Lamp

The heart of the optical tritium detector is the discharge source used to create the electronically excited

atomic hydrogen isotopes. A variety of discharge sources (electrodeless, r.f., d.c., and microwave) are known to efficiently produce the red hydrogen Balmer α emission. Molecular hydrogen emission is also created and observed. One will have to determine the best discharge for use and optimize the lamp operation by adjustment of pressure, field strength, and temperature. The latter operating parameter is of considerable concern as the plasma temperature must be maintained as low as practicable to minimize temperature Doppler broadening effects in the emission.

4.3.2.4 Detection

The scanning Fabry-Perot etalon spectrometer is the system of choice to disperse and detect the Balmer α emission from the discharge source. This detection scheme offers considerable cost and physical space saving over the use of monochromators. Lenses will be used to sample a portion of the discharge region and to collimate the light. Filters may be used to eliminate unwanted lines before the Fabry-Perot etalon. Filters to pass the Balmer α lines are available at modest cost with sufficiently high transmission for the purpose. The collimated light then impinges on the etalon. This instrument functions in the following manner. It consists of two highly reflecting parallel plates. Due to interference, the plates transmit only at wavelengths corresponding to $\lambda_0 = (2nd/m) \cos r$ where n is the index of

refraction between the plates, d is the plate separation, m is a particular order number of the etalon, and r is the angle of inclination on the plate. If r = 0, $\lambda_0 = 2nd/m$. For a given order, m', as d is varied the equation $m'\lambda_0 = 2nd$ must hold. Therefore, λ_0 must change. In this way we can monitor the wavelength by simply changing the plate separation. This is most easily accomplished by a piezo-electric device which scans the distance as a function of applied voltage. Therefore, we can tune to the appropriate line (H_α, D_α, or T_α) by varying the voltage, or we can ramp the voltage (on timescales on the order of a few milliseconds) to obtain all three intensities. Of course, some interfacing to an oscilloscope or multichannel analyzer will be necessary, however, to monitor the resonances. Typically, a Fabry-Perot Etalon Spectrometer has a Finesse defined by

$$\frac{\Delta\lambda}{\delta\lambda} = \text{Free spectral range/bandwidth}$$

We wish to observe lines separated by $\tilde{\sim}6$ cm^{-1}, therefore, our minimum free spectral range should be ≥ 6 cm^{-1}. Also we wish to resolve lines separated by the difference between T_α and D_α without resolving the hyperfine components of either set (although one could, in principle, obtain the same information by resolving the hyperfine structure as well). Therefore, we need a bandwidth of ~ 0.5 cm^{-1}. This will easily allow separation of the various isotopic features and yet not resolve the structure of their

individual hyperfine lines. The finesse must then be $\geq 6/.5 \approx 12$. Since $F \geq 12 = \pi/1-R_1$ where R_1 is the reflectivity of the plates, R_1 must be $\geq$ 74%. It should be pointed out that when Fabry-Perot is tuned through one of its orders, the transmission of light approaches 100% and so virtually all the collected light may be monitored. By using the Fabry-Perot we can then observe the amount of light occurring for any given isotope of hydrogen and can ratio this against either a known amount of hydrogen, or simply against the amount of hydrogen in the airstream itself if a relative amount is all that is required.

Once the light is imaged on the photomultiplier tube, we may send the signal to a strip chart recorder, oscilloscope, or, in the case where one wishes to observe all three isotopes as a function of applied voltage, to a multichannel analyzer which can add successive scans to enhance the signal-to-noise ratio.

4.4 SENSITIVITY OF PROPOSED DETECTOR

It is appropriate to consider what the minimum detectable signal (i.e., that which produces a signal-to-noise ratio of one) would correspond to in terms of the concentration of tritium atoms. In order to calculate this, we need to know the solid angle of light we can expect to collect, the filter efficiencies, photomultiplier sensitivity and the volume of the sample cell actually viewed by

the photomultiplier and imaging optics. These quantities can be calculated approximately.

First, assume that we can use the Equivalent Noise Input for the photomultiplier tube. This is typically $\sim 1 \times 10^{-15}$ watts/Hz)$^{1/2}$. Therefore, $10^{-15} = N^{v}_{min}\ h\nu A/\Delta f)^{1/2}$ where A is the Einstein coefficient for spontaneous emission ($\sim 10^{9}$ sec^{-1} for Balmer α), $h\nu$ is the energy per photon for the transition observed ($\sim 3 \times 10^{-19}$ joules), (Δf) is the electronic bandwidth of the detection system, and N^{v}_{min} is the minimum number of molecules actually observed. This can be related to $N_{min} \times V$ where N_{min} is the minimum number density we can detect for a particular sampled volume, V. Using f-1 optics, one can view a fractional sample of 1/16 of the spherical flux. From previous work on iodine monitoring and C_2 monitoring in flames, we can conservatively estimate a sampled volume of 10^{-4} cm^3. Therefore,

$$10^{-15} = N_{min}\ 10^{9} \times 10^{-4} \times 1/16 \times 3 \times 10^{-19} / (\Delta f)^{1/2}$$

$$\text{so } \frac{N_{min}}{(\Delta f)^{1/2}} = 5 \times 10^{-1}$$

We immediately see that in order to gain maximum sensitivity, one wishes the bandwidth ($\sim$1/counting time) to be as small as possible. Assuming a reasonable modulation of 100 Hz, $(\Delta f)^{1/2} = 10$ gives $N_{min} = 5$ atoms/cm^3. Until this point we have not included such factors as filter

efficiencies nor the amount of light sampled after the Fabry-Perot (which depends upon the mode of operation). We can estimate that such factors are on the order of 1/100. Therefore, $N_{min} \approx 500$ atoms/cm^3. As was noted, this can be as high as 5×10^4 atoms/cm^3 given the uncertainties required in our calculations. One may compare this to concentrations present in reprocessing facilities. From information supplied by Dr. Bob Girton of Allied Chemical at Idaho Falls, an estimate of 8×10^9 atoms/cm^3 maximum concentration was obtained for stack gas effluents during reprocessing. Measured values during some of their processing runs often fall 10^3-10^4 times lower. Therefore, we may need to routinely detect 8×10^5 atom/cm.^{3} As can be seen, our estimate of 5×10^4 which conservatively allows for all uncertainties makes this technique a viable candidate for development as a real time diagnostic for tritium concentration measurements. The primary advantage of the optical diagnostic technique over radio-counting techniques results from the fact that all the tritium atoms present are available for optical detection. A well designed optical detector may even be able to sample a given tritium atom many times during a given measurement. Alternatively, radio-counting techniques are limited to measuring only those atomic nuclei which decay during the measurement period. In a typical measurement period (perhaps of a few seconds) the

probability that an atomic specie with a several year half life will decay and produce a β particle for measurement is very low.

4.5 TRITIUM MONITOR PROGRESS

The level of funding for the tritium detector project (25% of that requested) during FY-78 has limited the progress of this task. We have concentrated upon areas of research and development which did not require signigicant expenditure for equipment. Nevertheless, significant progress has been made in specifying components to be used in the detector and in making experimental measurements critical to the design and operating parameters. We feel that progress during FY-78 has allowed us to demonstrate the proof of principle involved in the concept. The components are sufficiently specified at this point to allow the immediate fabrication of a breadboard detector during FY-79 assuming funds allow the required parts procurement. We will now review the progress made in FY-78 on each of the component building blocks for the optical tritium detector.

4.5.1 Tritium Catalytic Oxidizer

This is an area of development which has been diligently pursued by the nuclear industry for many years. The catalytic oxidizer system to be used will depend to some extent upon the composition of tritiated species to be oxidized. It is anticipated that the majority of tritium

effluents to be measured will be in the form of HTO and HT. Bixel and Kershner[19] have carefully studied the catalytic oxidation of HT using Pt-Pd catalyst as a function of temperature. For Engelhard No. 50088 catalyst[20] in their studies they obtained a first-order rate of 2.27×10^5 liter/sec-liter catalyst and a temperature dependent rate constant of

$$K = 2.27 \times 10^5 \, e^{-7100/RT}$$

Thus, a small bed catalyst operating in the region of 175°C will oxidize >99.9% of HT to HTO in a flowing airstream.[19] A tritium catalytic oxidizer to meet these requirements can be purchased off the shelf and used as a building block in the tritium monitor.[20]

These conditions are not severe enough to oxidize tritiated organics. If the effluent to be monitored contains significant tritium bearing organics, there are other catalytic conditions which can be used to oxidize these species.[2,19,21]

4.5.2 HTO Separator

For the purpose of laboratory measurements and breadboard detector design we have chosen to concentrate on the permeation distillation driers as sold by Perma Pure.[10] These separators will give a capability for continuous separation which will avoid batch operation. If sensitivity demands require, cryogenic or molecular sieve trapping techniques will remain a fallback for a concentrating method.

The permeation distillation membrane driers are claimed to be absolutely discriminating against all anticipated atmospheric components except water. The manufacturer claims[10] the concentration of NO_2, NO, CO, SO_2, N_2, O_2, H_2 and hydrocarbons in the counter current purge gase aqueous phase will be less than a few ppm. These levels should be adequate for operation of the discharge lamp. The operation of a permeation distillation drier will be tested by mass spectroscopic grab sampling in the counter current stream to determine discrimination against atmospheric components. It will then be tested in conjunction with the discharge lamp.

4.5.3 Discharge Lamp

As noted in the introduction, a wide range of discharge sources have been observed to give rise to resonance emission on the Balmer α emission lines of hydrogen. These include various versions of radio frequency, microwave, and electric discharge sources. A concerted literature search revealed that none of these systems has been optimized for Balmer α emission relative to molecular hydrogen emission.

Of more immediate concern is the determination of the lamp and operating parameters which will produce the lowest possible plasma temperature. This is required to avoid temperature broadening of the hydrogen and deuterium Balmer emission lines into the tritium emission region. This effect can be demonstrated for the following

hypothetical gas mixture. Assuming concentrations

$$H = 7 \times 10^{12} \text{ atoms/cm}^3$$

$$D = 1 \times 10^{9} \text{ atoms/cm}^3$$

$$T = 1 \times 10^{6} \text{ atoms/cm}^3,$$

we can compute the fluorescence intensity of the hydrogen isotope species at the tritium Balmer α line center. These numbers are given in Table IV.

TABLE IV

ISOTOPE EMISSION COMPONENT INTENSITY AT TRITIUM LINE CENTER AS A FUNCTION OF LAMP TEMPERATURE

Lamp Temperature	Emission Component		
T°K	H	D	T
300	9×15^{-6}	0.46	1.00
1000	1.4	7.0	1.00
3000	1190	57	1.00

As can be seen at lamp plasma temperature $\gtrsim$1000°K, it would likely be impossible to extract information concerning tritium concentrations from the tail of the hydrogen emission component for the hypothetical gas mixture assumed above.

We have evaluated several potential lamp sources to minimize the plasma temperature. The hollow cathode electric discharge design has proven to have almost ideal operating characteristics. Figure 8 shows typical operating characteristics for such a lamp at the given operating

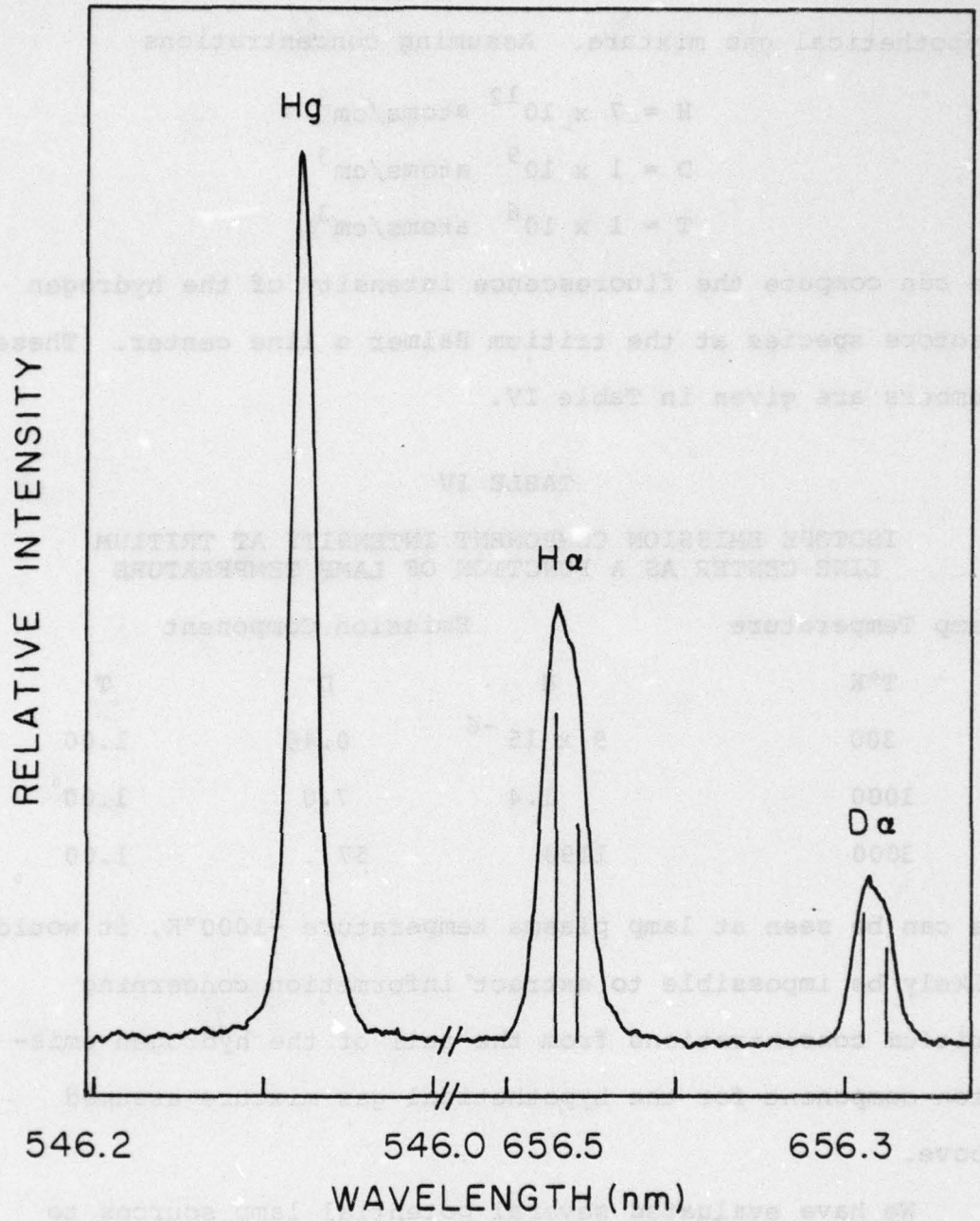


Fig. 8 - Spectrum of the Balmer α emission from an experimental hollow cathode lamp. The lamp is operating at a total pressure of 4.5 torr. The gas concentration ratios are $H_2/D_2/He = 0.6/0.3/35$. The lamp is operating at 13ma current at 13 kV. The spectra are scanned with a 0.5 m monochromator with an instrument resolution of 0.1 Å, as shown by the scan of the Hg 5461 Å line from a calibration lamp. The two major Hα and Dα hyperfine components are shown under each peak as vertical lines.

parameters. Within the limited resolution of the laboratory monochromator, the hydrogen and deuterium line widths deconvoluted from the hyperfine components are consistent with a plasma temperature near room temperature. Thus, we feel that this major component of the optical detector is now specified. The sensitivity of the detector has been demonstrated by using the highest available grade of He as the discharge gas for the lamp. Under these conditions the sub ppm impurity of H_2 in the He is sufficient to provide copious signal from H Balmer α for detection. The hollow cathode lamp has been shown to operate satisfactorily on the H_2O in He, as well as H_2 in He.

4.5.4 Projected Research

As detailed in Section 4.3.2.4, the Balmer α emission is to be measured using a scanning Fabry-Perot Etalon Spectrometer. The limitation on funding has not allowed us to purchase this instrument to evaluate with the resonance lamps. The specifications and operating characteristics of the instrument have been worked out in detail. The components should be procured during early FY-79 for use in evaluating the lamps and projecting the techniques for signal processing and data reduction.

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SECTION V

AN OPTICAL $^{14}CO_2$ DETECTOR

5.1 INTRODUCTION

5.1.1 Production Sources and Production and Release Levels World-Wide

With the continued world-wide growth of the nuclear industry there is a valid increasing concern as to the global impact associated with the discharge of the long-lived radio-nuclides. One of the most significant of these is Carbon 14. A concerted effort is being devoted to evaluate release limits, to control production, and to the development of cleanup techniques for this isotope. Various monitoring and measurement techniques are currently under development. Table V, based on data derived by Davis,[1] shows an evaluation of the production sources and levels associated with various power reactors.

TABLE V

PRODUCTION RATES OF ^{14}C IN SEVERAL REACTOR TYPES

	Carbon 14 Production Rates $Ci/GW_{(e)}$ Yr.			
Reactor	Coolant	Fuel	Moderator and Annulus System	Cladding and Structural Matter
BWR	4.7	17.6	-	43-60
PWR	5.0	18.8	-	30-42
LMFBR	-	6.3	-	12.8
ATGR	-	12	-	<190
Candu-540 MW	9	15	870	-
Candu-750 MW	10	20	547	-

The Carbon 14 exists in a variety of molecular species, typically as a mixture of CO_2, CO, and hydrocarbons. The ratio of these species varies strongly with the type of reactor system. For instance, Kuntz[2] reports that ^{14}C measured in PWR reactors exists mainly as hydrocarbons, while the production in BWR stations[3] is more than 90% in the form of CO_2.

Reprocessing plants represent a significant potential production source for ^{14}C also. For instance, a production is estimated in the range of 400-2200 Ci of ^{14}C per year for a LWR fuel reprocessing plant treating 1500 metric tons of heavy metal annually with a range of 40-240 ppb of $^{14}CO_2$ in a reference flow of 500 scfm off gas.[4]

Release rates from PWR and BWR stations have been measured to be in the region of 6-8 $Ci/GW_{(e)}$ year.[2,3] In the BWR stations this release is at levels up to several hundred picocuries/cm^3 of air.[5] ^{14}C release from the HTGR reprocessing facility has been evaluated by Snider and Kaye.[6]

5.1.2 Monitoring and Control Requirements

At this point no requirements have been issued relating to the monitoring and control of Carbon 14 effluents. A large body of literature[7-9] and studies[10,11] on the environmental impact of ^{14}C are now available, and it seems evident that requirements for the control and monitoring of ^{14}C releases will be formulated in the near future.

5.1.3 Carbon-14 Monitoring Methods

A carbon-14 radioactivity level of 100 pCi/cm^3 corresponds to a $^{14}CO_2$ concentration of 2.3×10^{-11} g/cm^3 or 3×10^{11} molecules/cm^3. In air this level of activity corresponds to a concentration of ∿10 ppb. Therefore, any real time detection technique with practical sensitivity must have routine detection capability in the range of 1-10 ppb. At the present time no such instrumentation exists. The only instrumentation currently available with near real time capability is conventional infrared spectroscopy. The practical detection limit for these instruments is ∿1 ppm. In addition, it is doubtful that this equipment can distinguish $^{14}CO_2$ from $^{12}CO_2$.

Several scrubbing techniques have been developed with greater sensitivity. The most sophisticated of these systems separates carbon-14 gaseous compounds with a gas chromatograph and measures them by radio counting[9]. This instrumentation is very expensive and too complex for routine use. More typically CO_2 is removed from feed streams by scrubbing with bubblers in a dissolving solvent followed by radio counting. This technique is tedious to use, subject to contamination by other radioactive species and has not yet proven effective at below the ppm range.[9]

The most reliable instrumentation for use at the sub ppm range currently involves use of a fractionating column

with nickel catalyst to convert carbon species to CH_4 followed by separation by gas chromatography with subsequent analysis by flame ionization detection.[9] This instrumentation has been used to measure carbon-14 at the 100 ppb level with an uncertainty of a factor of two.

It is apparent that none of the presently available analytical instrumentation is suitable for real time measurement of $^{14}CO_2$. Even the best techniques have a sensitivity limit near 100 ppb. The instrumentation is extremely sophisticated, quite expensive, and is unlikely to be applicable for routine use for widespread effluent analysis. A significant need exists for the development of a sensitive real time diagnostic which can be routinely used for air sampling measurements.

5.2 DEFINITION OF TASK

The interagency contract between DoE and NRL was modified at mid-year FY-78 to allow for a feasibility study of new detection techniques which might be applicable for $^{14}CO_2$ monitoring in the effluents of nuclear facilities. It appears that a 1-10 ppb sensitivity range is required. Current techniques involving scrubbing and radio counting or gas chromatographic separation with radio counting or flame ionization detection appear to fall short of this limit even with more and more sophisticated adaptations of the instrumentation. For this reason, we have

chosen to concentrate on the development of new optical diagnostic techniques. The following criteria were used for guidelines in evaluation of optical techniques:

a. Detection limits should be in the 1-10 ppb range for real time or near real time measurements.

b. Instrumental discrimination is required against interferences from other molecular or isotopic species.

c. The specified analytical instrumentation must have reliability and ease of operation consistent with routine use under a variety of conditions.

d. The specified instrumentation after commercialization should have an economic appeal superior to present or future competitive gas chromatographic or radio counting techniques.

5.3 SPECTROSCOPIC CONSIDERATIONS

Carbon dioxide does not exhibit characteristic resonance electronic transitions in the visible or ultraviolet regions and is not characterized by electronic emission processes. Therefore, electronic transitions are not easily accessible for diagnostic purposes.

The infrared vibrational transitions of CO_2 are well known and have relatively strong absorption coefficients compared to many infrared absorbers. The absorption of the isotopic species of ^{12}C, ^{13}C, ^{14}C, ^{16}O and ^{18}O in all possible combinations in CO_2 form quite complex

superimposed rovibrational sequences of band systems. Conventional infrared spectrometers are completely unsatisfactory to resolve these spectra and attain the sensitivity required over very large sample path lengths. High resolution spectra indicate that a spectral resolution of better than 0.05 cm^{-1} is required for isotopic analysis purposes.

There are several infrared laser sources which offer the potential of tunability and wavelength resolution in the region of CO_2 infrared transitions. These include:

a. High pressure tunable TEA CO_2 lasers which operate in the region of 10.6 μm.

b. High pressure CO lasers which operate in the region of 5 μm,

c. Optical parametric oscillators which are tunable across the near infrared region of the spectrum.

d. Tunable diode lasers which are tunable across the near and mid-infrared region of the spectrum.

Each of these sources was evaluated for potential use in measurement of CO_2 transitions. The tunable diode laser is the excitation source of choice. The CO_2 TEA laser is tunable but only over narrow regions near rotational line centers, and the laser does not operate on the ground state transition from which the overwhelming majority of CO_2 absorptions must take place. The CO TEA laser is only line tunable and could be used to pump only the

less strong of the CO_2 transitions. The optical parametric oscillator is truly continuously tunable and is capable of narrow bandwidth operation. The problem with the OPO lies in its complexity and expense. The OPO requires a separate laser to pump the parametric oscillator. These systems operate as laboratory instruments, but they have not yet reached the level of design technology which will allow their widespread use. They remain a possible option, however, for future applications requiring narrow band tunable capability in the near infrared.

5.3.1 Relevant Experiments with Diode Laser Spectrometers

Recently, significant advances have been made in the use of narrow bandwidth scanning diode lasers in conjunction with long path length absorption cells for trace gas analysis.[12,13,14] These tiny lasers are characterized by an extremely narrow bandwidth. They are temperature or current tunable over a considerable wavelength region and, because of their very low divergence, are readily adaptable to long (up to one km) path length cells.

Reid[12] and coworkers have used a scanning diode laser in conjunction with a 300 meter multiple pass cell to measure SO_2 concentrations in polluted atmospheres. The sensitivity limit in these experiments is reported as 3 ppb of SO_2 in air.

CO_2 exhibits a much stronger infrared absorption at $\sim$2350 cm^{-1} due to the ν_3 asymmetric stretching vibration. Recently, Wahlen, et al.[15] and Eng, et al.[16] have also used a scanning diode laser to study the high resolution spectra of isotopic CO_2. They report highly accurate measurements of the $^{14}C^{16}O_2$ line positions relative to those of $^{13}C^{16}O_2$ and $^{12}C^{16}O_2$. Figure 9 shows a trace of a portion of the spectrum taken near 2241 cm^{-1} by Wahlen, et al.[15] This spectrum taken by direct detection demonstrates the instrumental resolution. Note the complete separation of $^{14}CO_2$ features from those of $^{13}CO_2$.

The isotope shifts are well resolved among all of these species, and there are no apparent interferences in one of the rotational branches of $^{14}CO_2$ from the other isotopes. This indicates that $^{14}CO_2$ can be detected in the presence of $^{12}CO_2$ and $^{13}CO_2$. Moreover, from preliminary evaluation there do not appear to be any serious molecular interferences from other species.

To make measurements quantitative, one must know the value of the absorption coefficients of the various lines of importance in absorption. These can be measured experimentally or calculated.

Table VI adapted from Wahlen, et al.[15] demonstrates that good progress has been made with these evaluations.

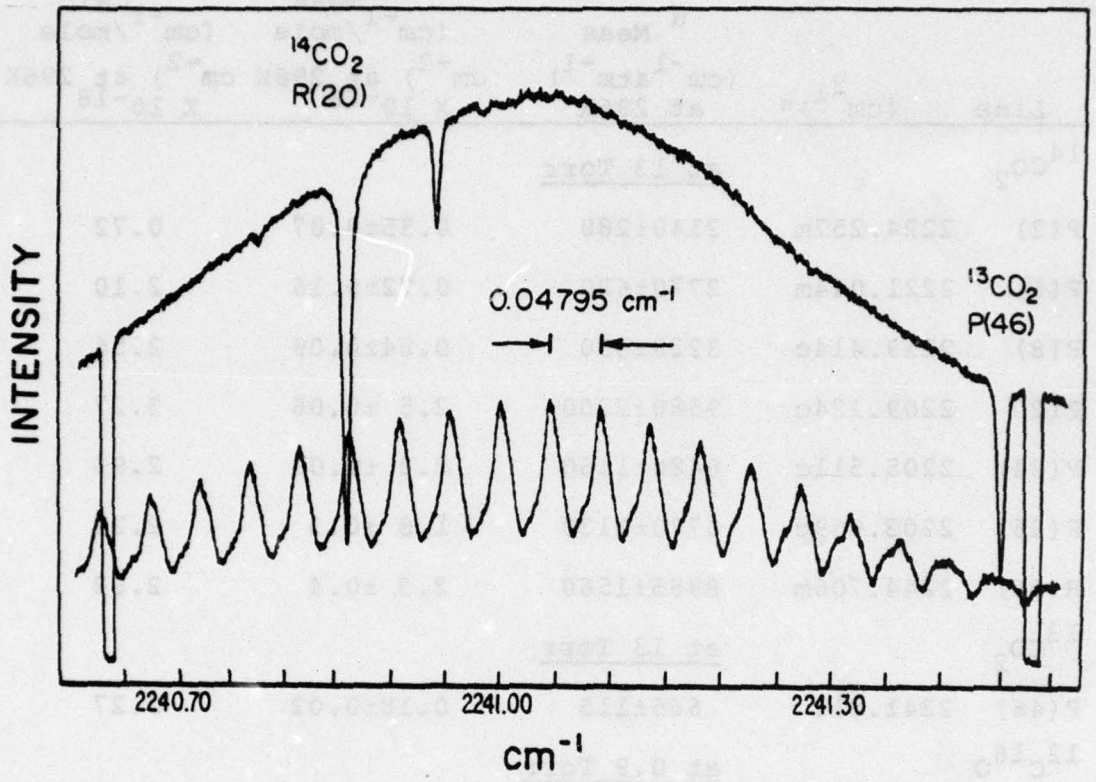


Fig. 9 - Spectral absorption scan near 2241 cm^{-1} showing the $^{14}CO_2$ R (20) and $^{13}CO_2$ P (46) lines. The unlabeled feature near the center of the scan is a $^{13}CO_2$ line at 2240.95/cm^{-1}. The lower trace shows an etalon fringe scan. The etalon free spectral range is 0.04795 cm^{-1}. These fringe patterns are used for wavelength calibration. This figure is adapted from Reference 15.

TABLE VI

ABSORPTION COEFFICIENTS AND LINE STRENGTHS OF $^{14}CO_2$

Line	ν_1 (cm^{-1})*	α Meas ($cm^{-1}atm^{-1}$) at 296K	S_{-1} Meas (cm^{-1}/mole cm^{-2}) at 296K X 10^{-18}	S_{-1} Calc (cm^{-1}/mole cm^{-2}) at 296K X 10^{-18}
$^{14}CO_2$		at 13 Torr		
P(2)	2224.257m	2140±280	0.55±0.07	0.72
P(6)	2221.044m	2770±620	0.72±0.16	2.10
P(8)	2219.414c	3220±350	0.84±0.09	2.54
P(20	2209.124c	9580±2300	2.5 ±0.06	3.27
P(24)	2205.511c	8480±1160	2.2 ±0.03	2.95
P(26)	2203.669c	6770±1130	1.8 ±0.3	2.28
R(26)	2244.706m	8985±1560	2.3 ±0.4	2.62
$^{13}CO_2$		at 13 Torr		
P(46)	2241.511	665±115	0.18±0.02	0.27
$^{12}C^{16}O$		at 0.9 Torr		
R(23)	2227.639	59±6	0.018±0.002	0.013

* m = measured; c = calculated.

Because spectra under experimental conditions will likely be crowded with lines from several isotopically substituted molecules, one must know with confidence the line positions and assignments of the appropriate species. Table VII, adapted from Eng, et al.,[16] and Table VIII show measured and calculated frequencies for assignments for $^{14}CO_2$, which are in excellent agreement.

TABLE VII

MEASURED $^{14}C^{16}O_2$ ν_3 BAND ROTATIONAL LINES

Transition	Frequency (cm^{-1})	Reference Line	Reference Line Freq. (cm^{-1})
P(2)	2224.257±0.005	$^{12}C^{16}O$ R(23) (1 ← 0 BAND)	2224.713
P(4)	2222.660±0.010	$^{14}C^{16}O_2$ P(2) ($00^01 \leftarrow 00^00$ BAND)	2224.257
P(6)	2221.044±0.005	$^{12}C^{16}O$ R(22) (1 ← 0 BAND)	2221.749
R(10)	2234.012±0.01	$^{13}C^{16}O_2$ P(42D) ($01^11 \leftarrow 01^10$ BAND)	2233.859
R(12)	2235.430±0.01	$^{13}C^{16}O_2$ P(52) ($00^01 \leftarrow 00^00$ BAND)	2235.129
R(20)	2240.878±0.01	$^{13}C^{16}O_2$ P(46) ($00^01 \leftarrow 00^00$ BAND)	2241.511
R(24)	2243.448±0.01	$^{13}C^{16}O_2$ P(44) ($00^01 \leftarrow 00^00$ BAND)	2243.592
R(26)	2244.701±0.01	$^{13}C^{16}O_2$ P(31C) ($01^11 \leftarrow 01^10$ BAND)	2244.831

TABLE VIII

CALCULATED $^{14}C^{16}O_2$ ν_3 BAND LINE POSITIONS

Transition	Calculated Freq. (Eq. (1)) (cm^{-1})	Calculated Freq. Minus Observed Freq. (cm^{-1})
P(30)	2199.924	
P(28)	2201.804	
P(26)	2203.664	
P(24)	2205.502	
P(22)	2207.318	
P(20)	2209.113	
P(18)	2210.885	
P(16)	2212.635	
P(14)	2214.363	
P(12)	2216.068	
P(10)	2217.750	
P(8)	2219.409	
P(6)	2221.046	+0.002
P(4)	2222.659	-0.001
P(2)	2224.249	-0.008
R(0)	2226.591	
R(2)	2228.123	
R(4)	2229.632	
R(6)	2231.118	
R(8)	2232.580	
R(10)	2234.019	+0.007
R(12)	2235.435	+0.005
R(14)	2236.828	
R(16)	2238.198	
R(18)	2239.545	
R(20)	2240.869	-0.009
R(22)	2242.171	
R(24)	2243.450	+0.002
R(26)	2244.707	+0.001
R(28)	2245.942	
R(30)	2247.155	

In the experiments of Reid, et al.[12] on SO_2, mentioned above, second harmonic detection was employed using a modulated diode laser. The detector is of standard infrared design coupled to a standard lockin amplifier. The use of this type of detection scheme significantly enhances the signal-to-noise ratio and hence the detectability. In addition, it converts spectra to a presentation with a flat baseline. Figure 10 demonstrates[12] the use of this technique for measurements on SO_2.

5.4 PRACTICAL LIMITS OF SENSITIVITY

The detection limits which can be achieved using infrared scanning diode lasers in conjunction with long path length white absorption cells depends upon several factors. The more important of these include the following:

a. The availability of scanning diode lasers in the wavelength region required for specific transitions,

b. the line strengths of the transitions to be measured,

c. finding regions of the spectrum suitably free from interferences by other isotopic or molecular transitions, and

d. the design of a sensitive and rugged detection scheme which is capable of automatic scanning of the transition of interest.

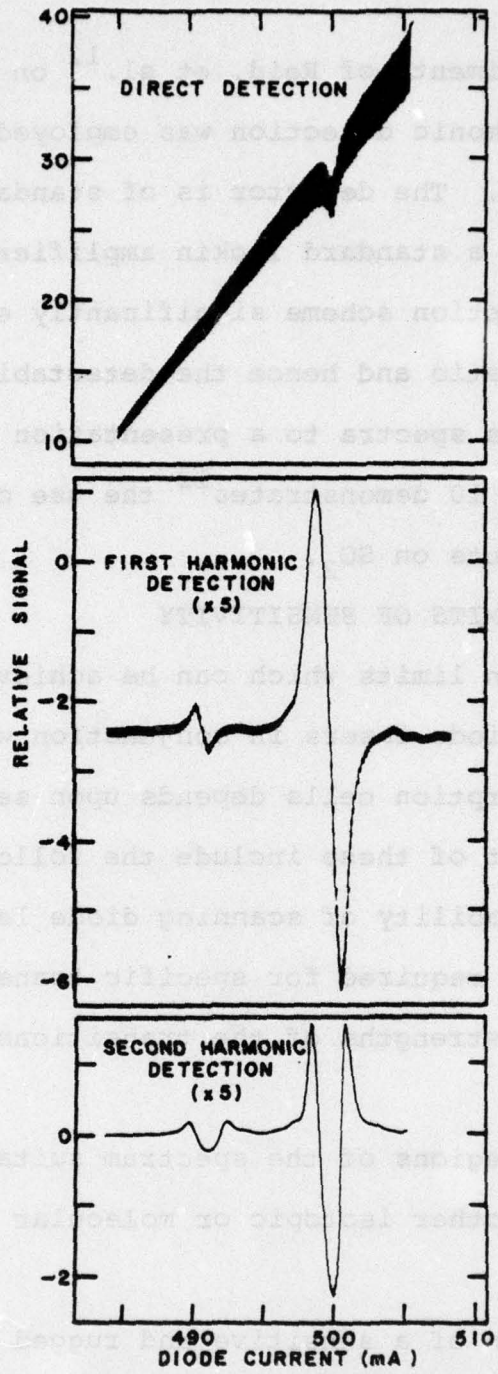


Fig. 10 - These plots demonstrate three detection schemes for scanning infrared laser diode absorption spectra. The three traces are taken under identical experimental conditions monitoring a transition in SO_2 gas at low pressure. The dramatic noise reduction in the spectra is apparent with the second harmonic detection scheme. This figure is adapted from Reference 12.

Using second derivative detection with presently available laser diodes and a 300 m White cell, Reid[12] has evaluated the minimum detectable concentration limits for several molecules. These values are shown in Table IX adapted from Reference 12.

TABLE IX

MINIMUM DETECTABLE CONCENTRATION FOR MOLECULES OF ATMOSPHERIC IMPORTANCE

Molecule	Absorption Coefficient of Strong Lines ($m^{-1}ppb^{-1}$)	Approximate Wavenumber of Lines (cm^{-1})	Sensitivity (ppb)
SO_2	3.5×10^{-8}	1140	3
O_3	2×10^{-7}	1050	0.5
N_2O	5×10^{-8}	1150	2
CO_2	3.5×10^{-10}	1075	300
H_2O	2×10^{-9}	1135	50
NH_3	2×10^{-6}	1050	0.05
PAN	$\sim 3 \times 10^{-7}$	1150	$\sim$ 0.3
CH_4	3×10^{-6}	1300	0.03
SO_2	3.5×10^{-7}	1370	0.3
NO_2	5×10^{-6}	1600	0.02
NO	3×10^{-6}	1880	0.03
CO	10^{-5}	2120	0.01
CO_2	10^{-4}	2350	0.001

Reid estimates a detection sensitivity with his apparatus for CO_2 of <0.001 ppb. We concur with Reid's evaluation. We estimate that easily made improvements in Reid's apparatus and techniques can account for another factor of thirty in detection sensitivity. This should place the minimum detectable level for $^{14}CO_2$ at $\lesssim 3 \times 10^{-5}$ ppb. Note that this detection limit corresponds to an atmospheric sample, not a scrubbed sample. However, it should also be noted that these measurements were made at ten torr total pressure to minimize line broadening. Measurements at low pressure on flowing airstreams do not represent a problem in the design of an analytical monitor.

5.5 CONCLUSIONS AND RECOMMENDATIONS

Evaluations of the requirements in nuclear applications indicate that a successful optical detector for $^{14}CO_4$ must have a sensitivity in the range of 1 ppb in air.

An evaluation of the scanning diode laser used in conjunction with a White cell and second derivative detection indicates a detection sensitivity for $^{14}CO_2$ of $<10^{-4}$ ppb. This is for real time monitoring on flowing airstreams. It should be possible to extend this level of sensitivity by several factors of ten by using cryogenic trapping of CO_2 if the need ever arises for more sensitive detection. It is overwhelmingly obvious at this point that real time optical detection of airborne $^{14}CO_2$ at currently existing

levels is a practical goal using scanning diode lasers. This technique offers obvious advantages over the currently used methods for measuring Carbon-14.

We strongly recommend that this technique be vigorously developed for specific application to measuring Carbon-14 in atmospheric effluents associated with nuclear applications. If so pursued, it is very likely that this instrumentation will become the analytical technique of choice for widespread application.

5.6 FURTHER CONSIDERATIONS

Although the development of this optical diagnostic for $^{14}CO_2$ represents a moderate economic investment, the required instrumental costs will likely be considerably less than that currently required for cryogenic trapping, gas chromatographic separation and radio counting. In addition, one would have the advantage of continuous real time monitoring capability.

A possibility exists that a single scanning diode laser spectrometer will have a useful sensitivity for several species in addition to $^{14}CO_2$. These include ^{14}CO, $^{14}CH_4$, NO_2, N_2O, and HTO. Each of these species will have to be considered based upon the following criteria:

a. wavelength scanning range of the diode laser,

b. resonant frequencies of molecular isotopes,

c. possible isotopic and molecular interferences, and

d. transition strengths of the vibrational resonances to be probed.

Although it is not presently possible to give detection limits for these species, they all fall into a wavelength region which makes them potentially attractive for monitoring.

Further laboratory research using the scanning diode laser spectrometers is necessary to make the relevant determinations of application for these other species. It is particularly important that this study be carried out because of the possibility of using the same instrumentation for measurement of tritium in off-gas effluents.

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SECTION VI

TESTING OF NEW HEPA FILTER MATERIALS

6.1 BACKGROUND

For a number of years the Naval Research Laboratory has been cooperating with the Department of Energy in doing research on matters related to air filtration. Reference (1) constitutes the current statement of the agreement relating to this research. This report describes the status of the evaluation of several new materials and formulations for construction of filter materials. There are current efforts under study in DoE and the industry to improve aerosol filter papers in their resistance to attack by hydrofluoric acid vapors.

6.2 FILTRATION STUDIES

An all-glass filter paper typically contains a variety of sizes of microfibers. The relative amounts of these different sized fibers determine the aerosol filtration and air resistance properties of the finished filters. There are also quantities of coarser fibers made from chopped yarns, which add mechanical strength to the filter sheet. The Johns-Mansville (J-M) A-10 chopped yarn fibers used in the present HEPA blends are rather coarse and stiff. They are 1/4 and 1/2 inches long and about 15 microns in diameter.

Most of the work to date has centered around substituting yarns for these coarse fibers which are highly

hydrofluoric acid resistant and smaller in diameter than the J-M yarns. These replacement fibers are organic materials and can constitute up to approximately 5% of the specified allowable 7% organic content of the filter medium. The remaining 2% of organics are required for the waterproofing compound. The use of these finer organic fibers are intended to improve the paper's mechanical strength and enhance the filter paper's flexibility and folding properties. The developmental work has involved both finding a satisfactory fiber blend and determining techniques to get suitable dispersions in the medium. A large number of papers have been made and tested to get a suitable reference base. To explore the possibilities of making organic fiber-containing sheets, commercial HEPA blends are used as a standard. Selected results of these studies are shown in Table X. The data in Table X show resistance, thickness, DOP penetration, and tensile strength, when available for these materials.

All of the experimental hand sheets reported on to date use a formulation substituting Owens-Corning (OC) "Beta" (β) fiber yarns for the previously used J-M yarns. The β fibers are longer (1/2 inch) and finer (3 to 4 microns diameter) than the J-M A-10 fibers.

The organic fibers when used were substituted for an equivalent amount of "Beta" fibers in all but one instance.

The exception was the SWP_R sample. This substitution was for an equivalent amount of code 104 (0.35μ diameter) glass fiber.

Satisfactory dispersions were achieved with gentle agitation and a minimum of rotary cutting or other destructive action. Dispersions were made successfully using a magnetic stirring bar and an ultrasonic probe. An acid pH(ca 3.0) was necessary. Visual inspection of the filter medium and the resulting hand sheet data showed rather good dispersion of the different organic fibers. Resistance and smoke penetration performance of the hand sheets was generally satisfactory and met specification requirements.

A series of hand sheets are being sent to Mr. K. Terada - 750, Atomics International Division, Rock Flats Plant, P. O. Box 464, Golden, Colorado 80401, for the hydrofluoric acid (HF) exposure effects and resultant resistance changes. To date, a partial shipment has been sent and will be reported on at a later date. Candidate materials selected and determined adequate for testing are as follows:

a. Control Sheet (With JM-A10 fiber)

b. M-124 Control (With OCβ fiber)

c. Poly Fiber - Crown Zellerbach's SWP_R synthetic fiber

d. Carbon Fiber - Standard fabric type

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e. Kenlar - Kenlar is duPont's registered trademark for its aramid yarn.

Before completion of this problem two series of hand sheets incorporating fibrids produced from yarn and floc of some high-temperature-resistant polyamide polymer will be fabricated and submitted for test.

6.3 SUMMARY

These studies have shown that satisfactory organic fiber-containing papers have been made, however, further work is required to seek a formulation which will give the best combination of desirable properties.

TABLE X

PERFORMANCE AND FORMULATION CHARACTERISTICS OF SELECTED FILTER PAPERS

Sample	Remarks	Resistance 14.2 cm/sec (mm H_2O)	Thickness TMI (Mil)	Fiber Diameter (Micron)	DOP Penetration H.2 cm/sec %	Tensile Strength 1" Width Lb.
Control	Contains J-M A-10 fiber (6.2%)	82	16.6	J-M (15)	0.008	0.49
Control	Contains OC "Beta" fiber (6.2%	95	17.2	β (3 to 4)	0.031	1.87
Poly Fiber	Contains 3.1% of Crown Zellerbach SWP_R synthetic fiber	118	15.5	-	0.01	-
Carbon Fiber	Contains 3.1% of carbon fibers	80	17.5	5	0.024	-
Kenlar[2] Fiber	Contains 3.1% of Kenlar[2] fibers	91	16.6	6	0.004	-
Y-100	Commercial paper supplied	77	20.5	-	0.026	-