**Study of the Atmospheric Chemistry of
Radon Progeny in Laboratory and Real Indoor Atmospheres**

Technical Report for the Period

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by

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Abstract

This report covers the first quarter of a year in which the two previous grants to Clarkson University (DE-FG02-89ER60860 and DE-FG02-89ER60876) have been combined into a single, continuing project. The chemical and physical behavior of the ^{218}Po atom immediately following its formation by the alpha decay of radon must be understood if the exposure to radon progeny is to be fully assessed. In order to pursue this general goal, two areas of radon progeny behavior will be studied; laboratory studies under controlled conditions to better understand the fundamental physical and chemical processes that affect the progeny's atmospheric behavior and studies in actual indoor environments to develop a better assessment of the exposure of the occupants of that space to the size and concentration of the indoor radioactive aerosol. Thus, two different sets of specific goals are set for this project.

The specific tasks of the controlled laboratory studies are 1.) Measure the neutralization rate of $^{218}\text{PoO}^+_2$ in O_2 at low radon concentrations, 2.) Determine the formation rates of $\cdot\text{OH}$, $\cdot\text{O}$, or other oxidative radicals formed by the radiolysis of air following radon decay, 3.) Examine the formation of particles by the radiolytic oxidation of substances like SO_2 , ethylene, and H_2S to lower vapor pressure compounds and determine the role of gas phase additives such as H_2O and NH_3 in determining the particle size, and 4.) Measure the rate of ion-induced nucleation in the sulfuric acid-water vapor system with and without NH_3 additions using a thermal diffusion cloud chamber.

The specific tasks of the exposure studies in occupied indoor spaces are 1.) Initiate measurements of the activity size distributions in actual homes with occupants present so that the variability of the indoor activity size distributions can be assessed with respect to indoor aerosol sources and general lifestyle variations of the occupants, 2.) Initiate a prospective study of the utility of measurement of deposited ^{210}Pb embedded in glass surfaces as a measure of the long-term, integrated exposure of the population to radon, and 3.) Acquire the components and begin to develop the methodology to determine the hygroscopicity of the indoor aerosol so that the changes in deposition efficiency of the radioactive indoor aerosol with hygroscopic growth in the respiratory tract can be assessed.

This report describe the initial efforts to achieve these objectives.

INTRODUCTION

The health effects of the radon decay products are strongly dependent upon their behavior in the indoor atmosphere. Particularly for ^{218}Po , the partitioning between the "unattached" state and the "attached" forms, combined with the preexisting aerosol particles, has a significant impact on the calculation of the dose to the lung resulting from a given decay product concentration. Thus, the chemical and physical behavior of the ^{218}Po atom immediately following its formation by the alpha decay of radon must be considered if its health implications are to be fully assessed.

At the time when the alpha leaves the nucleus, there are two excess electrons around the residual polonium nucleus. It is probable that the exiting alpha causes autoionization leading to a positive ion. The recoiling polonium nucleus has a recoil energy of 117 keV with a range in air of approximately 100 microns (Lind, 1961). The ion will be gas stripped to a moderate positive charge and then regain electrons as it slows toward thermal velocity such that at the end of the recoil path, 88% of the polonium atoms have a +1 charge and the remaining 12% are neutral (Wellisch, 1913; Porstendörfer and Mercer, 1979). The study of the neutralization behavior of the polonium ion has been a major focus of the initial efforts of this project. The results of these studies have been reported by Chu and Hopke (1988).

Other studies resulting from our previous DOE-supported programs have found that the $\cdot\text{OH}$ radicals produced by the deposition of energy into the air by the radon decay can oxidize SO_2 to $\text{SO}_4^{\cdot-}$ with observable particle formation (Hopke and Ramamurthi, 1988). Thus, the decay of radon modifies the atmospheric environment in which the radioactive is present. It is the further study of these modifications that are the primary interest of this project.

LABORATORY STUDIES

The principal areas of the laboratory studies are 1.) Measure the neutralization rate of $^{218}\text{PoO}^+_2$ in O_2 at low radon concentrations, 2.) Determine the formation rates of $\cdot\text{OH}$, $\cdot\text{O}$, or other oxidative radicals formed by the radiolysis of air following radon decay, 3.) Examine the formation of particles by the radiolytic oxidation of substances like SO_2 , ethylene, and H_2S to lower vapor pressure compounds and determine the role of gas phase additives such as H_2O and NH_3 in determining the particle size, and 4.) Measure the rate of ion-induced nucleation in the sulfuric acid-water vapor system with and without NH_3 additions using a thermal diffusion cloud chamber.

We are in the process of measuring the activity size distributions for a number of combinations of SO_2 and H_2O concentrations. These studies will comprise the MS thesis research project of Mrs. K. Karpen-Hayes. Mrs. Karpen-Hayes is supported by a teaching assistantship in the Department of Chemistry. We currently expect all of the laboratory studies to be completed by the end of 1990. She is also collecting samples of the airborne SO_4^{2-} and measuring its concentration by ion chromatography. We anticipate these measurements will permit us to use the known rate constant for the reaction of $\cdot\text{OH}$ with SO_2 to provide an estimate of the $\cdot\text{OH}$ radical production rate.

We have reestablished the system used while Professor Hopke's group was still at the University of Illinois to measure the $\cdot\text{OH}$ radical concentration through the chemical amplifier system of Cantrell *et al.* (1978). In this approach, the radon and water vapor are mixed with high concentrations of CO and NO. Chemiluminescent NO_2 is produced by a sequence of reactions that also produces another $\cdot\text{OH}$. Thus, through this catalytic reaction sequence, many NO_2 molecules are produced for each initial $\cdot\text{OH}$ radical. We have shown in prior reports the linear response we obtained with increasing H_2O concentration although we appeared to observe a limiting value of NO_2 molecules produced as we increased the ^{222}Rn concentration. We are now developing quantitative relationships between the light produced and the radon concentration and expect to be able to extract a hydroxyl radical production rate. Mrs. Huiling Ding is pursuing this problem as her Ph.D. thesis project. She is also working with Professor Y. Li of Clarkson University's Chemistry Department to develop a laser-induced fluorescence method that would permit the direct measurement of the $\cdot\text{OH}$ production rate.

Our other area of active development is the construction of a thermal diffusion cloud chamber (TDCC) (Katz, 1970) to study the rates of ion-induced nucleation caused by the ions produced by the radon decay. Mr. Yefei Wu, another Ph.D. student working on this part of the project, has corroborated the results of Daisey and Hopke (1990) that such ion-induced nucleation may be possible at VOC concentrations observed in indoor atmospheres based on the classical theory of J.J. Thompson (1906). He has furthermore used the more advanced theory of Suck (1982) that incorporates higher order electrical moment effects into the calculations which also suggest the formation of new particles by the ion-induced nucleation of commonly found organic compounds. A manuscript reporting these results is currently in preparation.

With respect to the construction of the TDCC, the vast majority of the system has been constructed. Only the temperature sensor holes need to be drilled and it will be ready for

assembly. The optical table needed for the droplet detection system has arrived and been placed in the laboratory and the He-Ne laser has also arrived. We still need to obtain the rest of the optical components that will focus and detect the scattered light and the heating and cooling systems that maintain the top and bottom of the chamber at their appropriate temperatures. The optical components will be ordered by the end of October and we hope to have the design of the heating and cooling systems completed by the end of November. Thus, we anticipate being able to test the chamber some time early in 1991. In addition, because TDCC have a reputation for being tricky devices, we have made arrangements to visit the laboratory of Professor Richard Heist at the University of Rochester in the near future to examine his system that is being used for photoinduced nucleation experiments. Finally, Professor J. Katz of the Johns Hopkins University has recently developed a flow TDCC system that he is going to use to study ion-induced nucleation and he has offered to cooperate with us, provide technical advice, and exchange results as both our systems begin to produce data.

Thus, the laboratory aspects of the project are generally underway. We have not reestablished the electrical mobility system developed by Chu (Chu and Hopke, 1988) to measure the neutralization rates. This item was deemed to be of lower priority and has been left to probably late in 1991 before we will get back to the problem of small ion recombination in ultrapure support gases.

REAL ATMOSPHERE STUDIES

The specific tasks of the exposure studies in occupied indoor spaces are 1.) Initiate measurements of the activity size distributions in actual homes with occupants present so that the variability of the indoor activity size distributions can be assessed with respect to indoor aerosol sources and general lifestyle variations of the occupants, 2.) Initiate a prospective study of the utility of measurement of deposited ^{210}Pb embedded in glass surfaces as a measure of the long-term, integrated exposure of the population to radon, and 3.) Acquire the components and begin to develop the methodology to determine the hygroscopicity of the indoor aerosol so that the changes in deposition efficiency of the radioactive indoor aerosol with hygroscopic growth in the respiratory tract can be assessed.

In order to corroborate that our automated, semi-continuous, graded screen array system functions as we believe it does in the measurement of activity-weighted size distribution, we performed a series of intercomparison measurements with personnel from the Environmental

Measurements Laboratory in Princeton House No. 31 during the period of August 21-23, 1990. These experiments were observed by D. van Cleef and R. Mosely of the U.S. Environmental Protection Agency. The activity size distributions were measured under background conditions and in the presence of particles generated by large particle sources (cigarette smoke) and small particle sources (electrical space heater and a propane torch). The agreement between the EML and CU values was extremely good and an abstract has been submitted to the EPA radon conference to be held in Philadelphia in April 1991. Measurements have also been made in the basement of a house in Shrewsbury, MA. This house is equipped with a RAdsorb activated carbon system for radon control and electronic air cleaner for particle control. The effect of these control systems on the activity size distributions produced by active aerosol particle sources was examined. The analysis of these data are still in progress, but we anticipate a presentation at a meeting to come from these studies.

In order to reduce the noise from the pump in living areas of a house, we have ascertained that the system will work with a 15 m separation of the pump from the manifold that directs the flow from the sampler/detector units. Using very heavy wall 0.75" S.d. vacuum hose, we have a sufficient conductance to maintain a large enough pressure differential to keep the orifices critical. Thus, we can separate the pump from the samplers. We are planning to go into Princeton house no. 31 within the next several weeks to make a series of measurements when it is occupied. The occupants of this house do smoke and it will give us the first opportunity to assess the exposure of smokers to radon progeny under normal living conditions. We anticipate mounting at least one other field sampling campaign before the end of the current contract period. For these experiments, we are hoping to find a home in the greater Syracuse, NY area in order to reduce the travel requirements that sampling in Princeton bring. The field sampling experiments are being conducted by the post-doctoral associates, Drs. Piotr Wasiolek and Nathalie Montassier.

Our design for the measurement system has raised sufficient interest that we have been asked to duplicate it for Pacific Northwest Laboratories and the U.S. E.P.A. Thus, we are currently building two systems at their expense similar to our original design and should have them completed before the end of 1990. Thus, DOE's investment in this instrument's development is leading to its greater utilization in radon-related research studies.

With regards to the measurement of ^{210}Po in glass using pulse ionization chambers, we have discussed chamber design with Dr. Christer Samuelsson of University Hospital, Lund,

Sweden. Dr. Samuelsson and a colleague will visit Potsdam following the Hanford Symposium on Health and the Environment that this year focussed its attention on radon. Thus, we anticipate developing a final design for a counter by the end of November 1990 and having it ready to test by then end of the current contract period. Thus, we will need the electronics modules requested for the next budget period in order to test and refine our design. Dr. Wasiolek is assisting with this effort.

We have begun discussions with a variety of Federal and State officials who deal with the public on the radon issue to assist our efforts to find volunteers who will place virgin glass samples in their homes for a period of 18 months. We plan to put out up to 4 pieces of glass per home in which two pieces would be placed in the room with the commonly watched TV set (one on an inside wall, one on an outside wall) and two pieces would be placed in the master bedroom (again one outside wall and one inside wall). We will try to get the glass samples placed as soon as possible to permit the longest possible exposure period to be available.

The final task of this portion of the project is the development of the tandem differential mobility analyzer (TDMA) system to measure the hygroscopic growth of the indoor aerosol when it encounters >95% relative humidity at 37°C. This is the Ph.D. thesis problem of Wei Li. It is not a trivial task to humidify air to this high level. We are currently exploring several design options and have talked with the U.S. scientists who have done most of the studies using this technique. We have obtained several helpful suggestions from Professor R. Flagan of the California Institute of Technology. He and his student had previously been very helpful in adapting our previous differential mobility analyzer (DMA) system to a scanning system as described in Wang and Flagan (1990). By ramping the voltage on the DMA, it is possible to scan through a size spectrum in about 90 seconds instead of 12 minutes via the conventional DMA stepped voltage approach. By speeding up the analysis portion of the TDMA, it makes it more likely that a complete hygroscopicity analysis can be completed before there is a substantial change in the nature of the indoor aerosol. We hope to have a prototype humidification system designed and built by the end of the current contract period. Dr. Montassier is helping in the development of the design of the humidifier and the construction of aerosol generation facilities that will permit us to test the TDMA system when fully assembled.

FUTURE RESEARCH PLANS

Because the first period of this contract was only 7 months and we are only 3 months of that into the contract, the future plans principally focus about completing the tasks describe above. With regards to laboratory studies, we anticipate that during this next year we will be able to measure the $\bullet\text{OH}$ radical production rates and from that information we will be able to make quantitative estimates of the importance of indoor radon to the free radical chemistry of the indoor atmosphere. We are also interested in the possible ion-molecule reactions that might be initiated by the deposition of the 5.5 MeV of energy from the radon alpha. We are just now gathering the background information on this problem, but we anticipate from some preliminary examinations that there could be a number of interesting reactions that result from the ionization and that further studies are warranted. The availability of new GC/MS and FTIR facilities within the Department of Chemistry at Clarkson make the examination of such reactions possible.

We expect that considerable time will be necessary to debug the thermal diffusion cloud chamber. Our initial work will be the duplication of prior homogenous nucleation results on simple hydrocarbons to insure that the system is performing satisfactorily. Once we are certain that the system is performing, then we will examine the ion-induced nucleation of those organic compounds that had the highest free energy of formation in our calculations of ion-induced nucleation based on both the Suck (1982) and Thompson (1906) theories. Since there are discrepancies between the two theories, the quantitative measurements of the nucleation rates that we will be able to make could help to resolve the discrepancies as well as add to the data base for future theoretical studies. Ultimately, we plan to look at the combined oxidation and nucleation mechanism to study the binary nucleation of water and sulfuric acid.

In our field studies, we expect to test the first pulse ionization chamber, insure that it is performing properly and then build the additional units to permit the efficient counting of the glass when it begins to return from exposure in the following year. As the counters come on line, we will be looking for opportunities to use the counters to measure artifacts in conjunction with ongoing epidemiological studies. We have indicated to the NJ Department of Health that possible counting time may be available and they indicated considerable interest in collaborating with us. Thus, we may be able to begin gaining data which can subsequently be fully evaluated when our prospective glass study has been completed.

We would hope to find 5 to 6 houses to study during the year in order to begin to measure activity size distributions in a series of normally occupied homes with oil versus gas heating, hot water versus forced air, gas versus electric stoves, absence or presence of woodstove

or fireplaces, use of space heaters (electric or kerosene), presence or absence of electrostatic air cleaners and/or humidifier on forced air systems, and effects of central air conditioning. In addition to the activity size distributions, we also plan to measure particle number distributions with the DMA and we hope to be able to measure deposition flux so that the room surface-to-volume ratio can be inferred. These additional measurements are by nature grab measurements, but they can provide the data to estimate the room model parameters necessary to better understand the dynamics of the radon progeny in the house.

Most of the year will be required to develop, assemble, and test the performance of the TDMA. There are a number of critical details that need to be included in the final instrument. For example, not only does the flow from the first DMA need to be humidified to cause the particle growth, but the sheath air in the second DMA must be heated and humidified to the same level to prevent evaporative loss within the second DMA. The effect of such high absolute humidity on the detector (electrometer or CNC) also needs careful study. Thus, we do not anticipate doing more than field trials of the TDMA system during the next year.

SUMMARY

We believe we are off to a good start on this combined project and have maintained the momentum of the previous efforts. We are moving along well with the development of new experimental systems while making maximum use of the systems we have previously perfected. We anticipate that by the end of the next year we will be well into the collection of substantial new data characterizing the behavior of the radon progeny both in the laboratory and in the real world.

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PROJECT PERSONNEL

Principal Investigator

Philip K. Hopke, Robert A. Plane Professor of Chemistry

Other Professionals

Piotr Wasiolek, Research Associate, July 1, 1990 - present.
Nathalie Montassier, Research Associate, August 1, 1990 - present.

Graduate Research Assistants

Huiling Ding, Research Asdsistant, July 1, 1990 - present.
Wei Li, Research Assistant, July 1, 1990 - present.
Yefei Wu, Research Assistant, July 1, 1990 - present.

PUBLICATIONS ARISING FROM THIS CONTRACT

Measurement of the Size Distributions of Radon Progeny in Indoor Air, P.K. Hopke, M. Ramamurthi, and C.S. Li, in *Aerosols: Science, Industry, Health, and Environment*, S. Masuda and K. Takahashi, eds, Vol. 2, Pergamon Press, Ltd, Oxford, 842-847 (1990).

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Measurement of Size Distributions of Indoor Radioactive Aerosols, C.S. Li and P.K. Hopke, submitted to the Proceedings of the 29th Hanford Symposium on Health and the Environment, Richland, WA, to be published by Battelle Memorial Press.

PRESENTATIONS OF RESULTS OF THIS CONTRACT

Measurement of the Size Distributions of Radon Progeny in Indoor Air, P.K. Hopke, M. Ramamurthi and C.S. Li, presented at Third International Aerosol Conference, Kyoto, Japan, September 1990.

The Effect of Air Cleaning on the Size of the Indoor Radioactive Aerosol, P.K. Hopke, C.S. Li, and M. Ramamurthi, presented at Third International Aerosol Conference, Kyoto, Japan, September 1990.

Air Cleaning and Radon Decay Product Mitigation, P.K. Hopke, C.S. Li, and M. Ramamurthi, presented to the 29th Hanford Symposium on Health and the Environment, Richland, WA, October 1990.

Measurement of Size Distributions of Indoor Radioactive Aerosols, C.S. Li and P.K. Hopke, presented to the 29th Hanford Symposium on Health and the Environment, Richland, WA, October 1990.

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