A study of the mechanism of formation of radon daughter aerosols

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ABSTRACT

The formation of radon daughter aerosols in air is found to be markedly influenced by the presence of charges and vapours. Experiments have been carried out with natural radon in the air to show that radon daughter products behave as single ions of high mobility in filtered dry air whereas they are attached to cluster aerosols formed in the presence of certain charges and vapours. In these experiments the cluster aerosols have been formed with ethanol vapour in the presence of small negative ions. Knowledge of this mechanism of attachment of radon daughters to cluster aerosols has also been used for the estimation of airborne radon. The radioactivity of these aerosols is studied by filtration through membrane filters. The degree of equilibrium between radon and its daughters in atmospheric air has been studied on the basis of this mechanism. The mechanism is of fundamental importance in understanding the nature of radon daughter products in the air under different environmental conditions.

1. Introduction

The attachment of radon daughter products to atmospheric aerosol particles is greatly influenced by the environmental conditions. A variety of complex processes are involved in the phenomenon of attachment. It is generally assumed that soon after their formation the radon daughters get attached mainly to aerosols in the submicron size range always present in the atmosphere in large concentrations. Finer details of the nature of attaching aerosol and the mechanism of attachment are not fully understood. The attachment mechanism is likely to be different for different environments. It is necessary to carry out detailed studies with different environmental conditions for a complete understanding of the processes involved.

The present study was carried out for finding the role played by negative charges and vapours in the formation of aerosols to which radon daughters can be attached. As a result of several experiments on the effects of passing ionized air over ethanol vapour we have been able to produce very stable molecular clusters to which radon daughters can be attached. A study of the formation of these clusters has provided important information on some of the likely phenomena of attachment of radon daughters to aerosols in the atmosphere; water vapour in the atmosphere playing a somewhat similar role as ethanol vapour in the controlled experiments.

Controlled formation of such clusters can also be used for accurate measurement of radon in air. This method of estimating radon has several advantages over the commonly used method of adsorption of radon on activated charcoal.

2. Attachment of radon daughters

Most of the recoil atoms from the decay of radon and its daughters are known to carry a positive charge. These recoil atoms behave like small positive ions in a gas and lose their charge by recombination with the negative ions in the gas. These recoil ions have about the same mobility in air as the positive ions produced in air.

We shall now consider the subsequent history of the initially positively charged radon daughters. These ions can be attached to negatively charged particles and surfaces, and also to

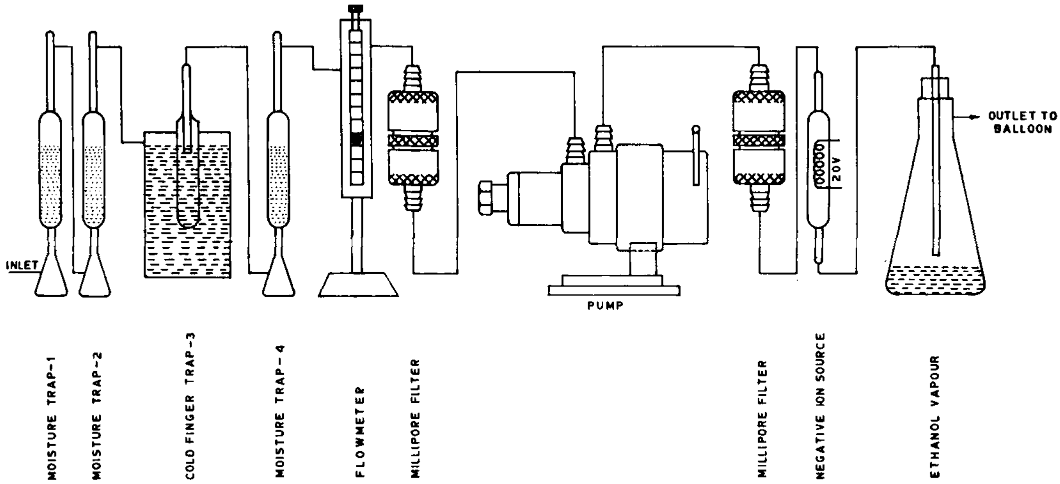

FIG. 1. Cluster aerosol generator for radon daughter attachment.

neutral particles and surfaces by inducing opposite charge in these. The normal ionization of the air leads to both negatively and positively charged ions, the latter being in excess.

Small ions have very large co-efficient of diffusion and very high mobility. These ions are rapidly attached to the surfaces of the reservoir when experiments on attachment are carried out with stored air. However, in the presence of certain vapours these ions give rise to large clusters of molecules having very small co-efficient of diffusion and very low mobility. We shall call these "Cluster Aerosols" in describing their mechanism of formation and their role in attaching radon daughters.

The present experiments are based on the controlled formation of cluster aerosols of ethanol vapour. The attachment of radon daughters to these clusters is allowed to proceed in an enclosed volume consisting of a large neoprene balloon.

3. Experiments

(a) Generation of aerosols for radon daughter attachment

Fig. 1 gives the basic experimental set up for the generation of cluster aerosols. The air is first passed through the moisture traps consisting of two magnesium perchlorate traps, a cold finger using dry ice dissolved in acetone, followed by another magnesium perchlorate trap. A millipore filter type-GS is used after the moisture traps to remove solid particles down to submicron size. An oil free suction pump specially cleaned to remove all impurities is used for drawing the air through the moisture traps and the millipore filter. A second millipore filter is used after the suction pump. The filtered and dried air is passed over a heated filament of kanthal for the production of negative ions. The air is finally passed through the flask containing ethanol before introducing it into the reservoir. The "cluster aerosol" is formed when the air containing negative ions passes over the ethanol vapour. The reservoir consists of a thoroughly cleaned neoprene balloon (Darex type J-11-18P-800). Negative ions are formed by the attachment of thermionically emitted electrons to electronegative gases present in the air.

A series of experiments were carried out by filling the natural atmospheric air in the neoprene balloon under different experimental conditions. The rate of filling was 10 litres per minute and total volume filled for each experiment was 300 litres. The air was allowed to stay in the neoprene balloon for an equilibrium time of 5 hours. The radon daughters attached to aerosols were subsequently filtered through a millipore filter type-AA and counted for alpha activity.

Fig. 2 gives the block diagrams of four different arrangements for the study of the behaviour of radon daughters. As shown in Fig.

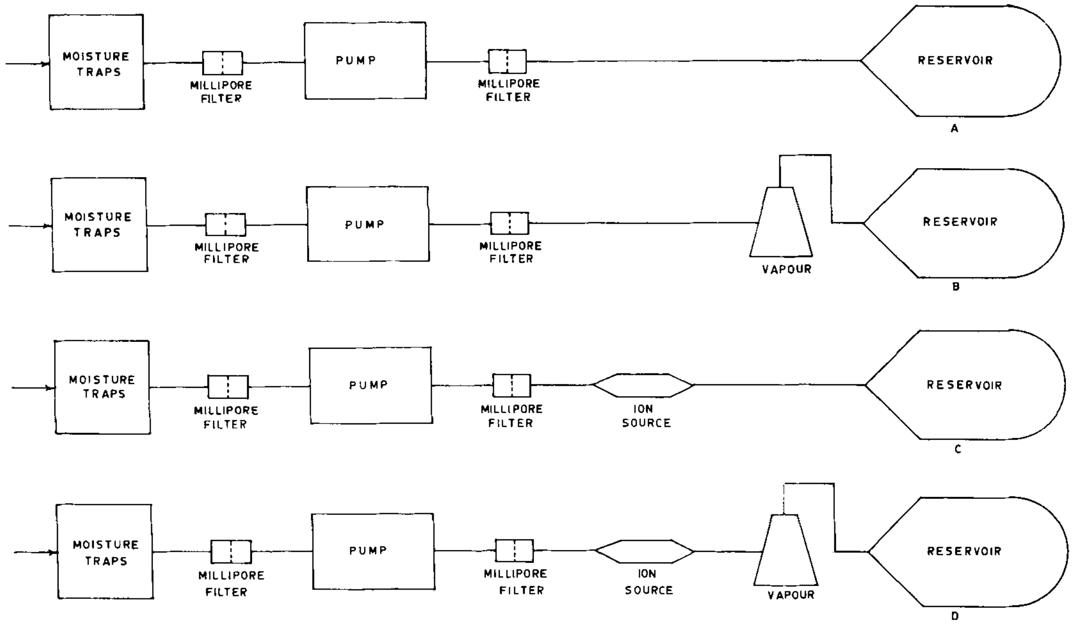

FIG. 2. Block diagrams of different filling systems for the study of attachment of radon daughters to cluster aerosols.

2A, if the air is completely dried and filtered through a millipore filter and filled in the neoprene balloon all the daughter product activity goes to the walls of the balloon. This is due to the fact that freshly formed radon daughter ions behave as small ions which diffuse rapidly and get collected instantaneously after their formation on the walls of the balloon. In this case when a sample is collected from the reservoir on a millipore filter type-AA no daughter product activity is found on the filter paper.

When the experimental set up is as shown in Fig. 2D all the activity of the radon daughters is found to be on aerosols which can be collected on the millipore filter with nearly 100% efficiency. In this set up the negative ions and ethanol vapour give rise to the formation of clusters of ethanol molecules, initially negatively charged. Experiments carried out with vapours in the absence of negative charges (Fig. 2B) showed that only about 5% of activity is collected on the millipore filter. This would show that the presence of vapours alone has no significant role in the formation of the cluster aerosols under consideration. When negative charges alone are present (Fig. 2C) only 10–20% of the activity is collected on the filter paper. Identical results were obtained with a negative ion source consisting of a cylindrical quartz tube lined inside with a semicylindrical zinc foil and illuminated with a mercury arc ultraviolet source. In this case negative ions are produced by the attachment of photoelectrons to electronegative gases. The concentration of negative ions and clusters used for the experiments was about 100,000 per cc of air.

These experiments show that the presence of small negative ions in the air helps in the formation of cluster aerosols. The stability of the cluster aerosols is an important criterion of their behaviour. It is important to note that these clusters are stable in the balloon with ethanol partial vapour pressure which is only 30% of the saturation vapour pressure. Whereas the clusters of ethanol molecules were found to be stable even for 15–20 hours, the clusters formed with water molecules in the undried air were found to be less stable. The stability of clusters with other vapours has not yet been studied.

(*b*) *Measurement of charge and mobility of small ions and cluster aerosols*

A teflon insulated parallel plate chamber was used for the measurement of charge and mobility of small ions and cluster aerosols.

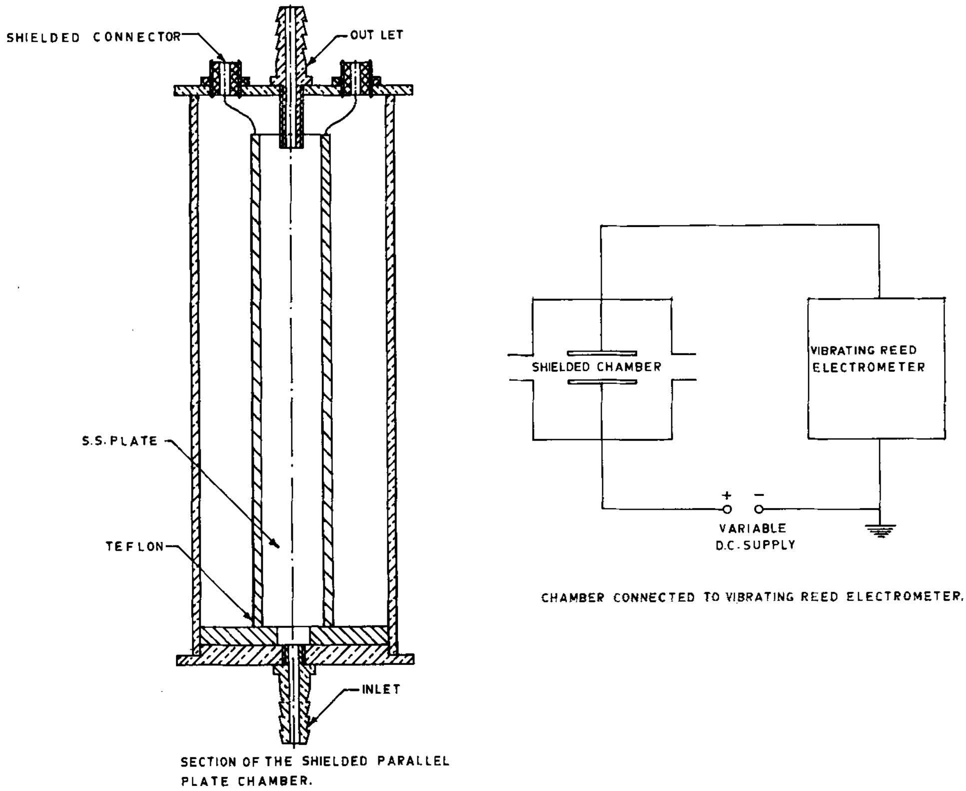

FIG. 3. Block diagram of the system for ion current measurement and section of the ion chamber.

Fig. 3 shows section of the chamber and block diagram of the charge measuring system. The parallel plate chamber with a rectangular cross section of 2.5 cm × 2.5 cm and 30 cm long is enclosed in a brass flow tube with an inlet and an outlet. The flow tube also serves as the outer shield of the chamber. The connections from the two plates are taken through teflon insulated shielded connectors. One of the plates is connected to the input of a vibrating reed electrometer. The other plate is connected to a variable DC power supply. The outer shield acts as the common earth for the electrometer and the power supply.

For the measurement of charge and mobility of the small ions the air passing over the heated kanthal filament is made to flow through the chamber. Fig. 4 gives a plot of the current obtained for different values of X, the field intensity. From this curve the upper and the lower limits of mobility were calculated and found to be 1.5 cm/sec/V/cm and 0.02 cm/sec/V/cm, respectively. With this set up it was not possible to measure the intermediate values of mobility.

For finding out the mobility of the cluster aerosols the negative charges on the cluster aerosols were collected on the collecting plate of the chamber at higher potentials. The collecting potential was increased from a very low value up to 3000 V. Saturation current was obtained at 2500 V, corresponding to field intensity X of nearly 1000 volts per cm. The negative ion current yielded by these clusters for different values of X has also been plotted in Fig. 4. From this curve the upper and the lower limits of mobility were found to be 0.02 and 0.001 cm/sec/V/cm.

In order to establish negative charge on the cluster aerosols a diffusion roll was devised for the collection of charges by diffusion. This consisted of 100 layers of closely wound aluminium foil of $2\frac{1}{2}''$ width. The foil was wound on a brass rod and placed inside a shielded perspex

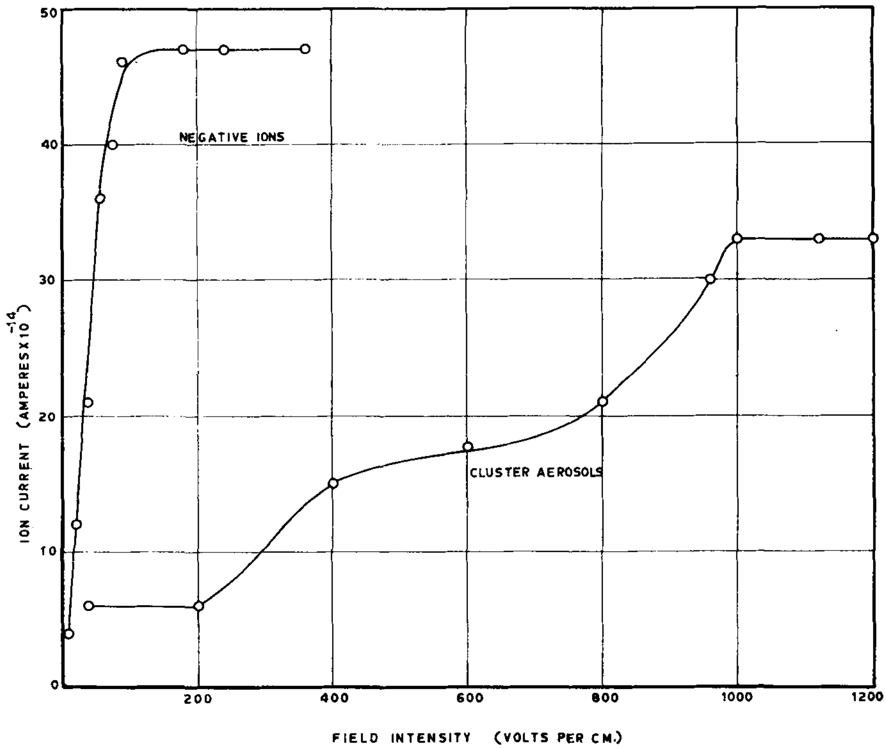

FIG. 4. Variation of ion current with field intensity for negative ions and cluster aerosols.

flow tube so that air could flow between different layers of the foil. The charge collected on the foil was measured by connecting it to the input of the vibrating reed electrometer through a shielded cable. Cluster aerosols were collected by this diffusion roll with nearly 100% efficiency.

(c) *The mechanism of attachment*

The mechanism may be explained as follows. In the air being filled in the ballon cluster aerosols are formed by the condensation of vapour around the negative ions when the air is passing through the flask containing ethanol, close to the surface of ethanol. This condensation has been found to take place even with the unsaturated vapour. The initial charge on these clusters is negative and their initial size is estimated to be between 0.01 to 0.05 micron as shown by the mobility measurements. In the air filled in the balloon the ethanol vapour pressure is only 30% of the saturation vapour pressure. The cluster aerosols survive at this vapour pressure. The negative charge on the clusters is lost rapidly, after filling in the balloon, but the clusters retain their identity even after the loss of this charge. These clusters behave like small condensation nuclei and grow to a stable size by coagulation. Although the stable size of the clusters has not been measured experimentally, it is large enough to prevent their attachment to the surface of the balloon by diffusion and small enough to prevent their loss by settling and is likely to be of the order of 0.1 micron. The radon daughters are attached to this aerosol soon after formation. The attachment probability is very high due to large population of the aerosols.

The probability for a radon daughter ion to attach to a cluster aerosol is proportional to the concentration of the aerosol. The number of attachment processes per unit volume per unit time is given by $\eta N n$, where η is the attachment co-efficient and N and n are the concentrations of aerosols and radon daughter ions respectively. The rate of formation of attached particles is given by

$$dN_s/dt = \eta Nn - N_s\lambda,$$

where N_s is the number of attached particles per unit volume and λ is the radioactive decay constant. At equilibrium

$$N_s/n = \eta N/\lambda.$$

The ratio N_s/n which represents degree of attachment is very large for larger values of N and smaller n as in the present case.

4. Measurement of radon concentration in air

In the experiments described above it has been shown that radon daughter products can be attached under controlled conditions to aerosols formed by ethanol vapours. Several experiments on the measurement of radon in the air carried out with these aerosols gave reproducible results. The accuracy of estimation of radon was also checked with radon from a standard radium solution of 500 $\mu\mu$C. This method of formation of cluster aerosols in the presence of vapours suggested interesting and useful applications in the measurement of radon, especially in the study of the degree of equilibrium between radon and its daughters at different locations.

The degree of equilibrium between radon and its daughters in the free air is often very uncertain and variable. A major part of the radon daughters in the free air is in the form of aerosol particles which can be retained on a millipore filter with a high efficiency. Therefore by direct filtration of the air through millipore filter the daughter product activity can be measured. By introducing an equal volume of air in a neoprene balloon after treatment by the method described earlier, and allowing the equilibrium to be attained inside the neoprene balloon, the equilibrium daughter product activity can be measured knowing the rate of sampling and the collecting time. Thus, by comparing the daughter product activity in directly filtered air and equilibrated air in the neoprene balloon it is possible to find out the percentage equilibrium in the free air. Actual studies have been made of the equilibrium conditions in the free air for different locations. Table 1 gives the results of studies of the ratio of directly observed to equilibrium activity studied with the present method under different environmental conditions.

5. Discussion

Although the condensation of vapours on charged nuclei in saturated and supersaturated vapours has been well established, very little is known about the mechanism of formation of molecular clusters in the presence of small ions in unsaturated vapours. The closest equivalent studies are those of LANGEVIN (1905) and POLLOCK (1915) on the formation of invisible clusters of water molecules in the form of large ions. The earlier belief that submicron solid particles are essential in the formation of such clusters was disproved by VASSAILS (1948) who found that no clusters were formed in highly filtered air containing water vapour but,

TABLE 1. *Ratio of normal radon daughter activity 'A' to equilibrium radon daughter activity 'B' in the air under different conditions.*

Expt. No.	Alpha activity in d.p.m.: Radon daughters in normal air A	Radon daughters in equilibrium B	Ratio A/B	Remarks
1	50.5	60.8	0.83	Inside laboratory winter season
2	75.0	125.0	0.60	Open field winter season
3	13.0	70.0	0.18	Open field summer season
4	9.2	58.0	0.16	Open field early morning of a summer day
5	8.0	120.0	0.07	Open field afternoon of a summer day
6	15.8	32.5	0.49	Open field evening of a summer day

when ultraviolet light was made to shine the charged nuclei produced by ultraviolet light gave rise to instantaneous formation of clusters of water molecules.

CHAMBERLAIN's (1956) observations on the behaviour of thoron daughter Th–B can be explained on the lines of our observations. He passed thoron mixed with air over a bunsen flame into a chamber and studied the deposition of Th–B on the walls of a cylindrical tube. He compared the results of deposition on the walls of the tube with and without bunsen flame and concluded that condensation nuclei formed in the bunsen flame helped in the attachment of Th–B formed by the decay of thoron. In this study the condensation nuclei of size few hundredth of a micron are shown to play an important role in the attachment of thoron daughters. These condensation nuclei are likely to be formed by the mechanism similar to the formation of cluster aerosols in our experiments.

The aerosols in the atmospheric air come from different sources, depending on the nature of environments. The formation of cluster aerosols in large concentrations is also likely under favourable conditions. These can be formed in the free air by the condensation of water vapour on natural negative ions (and also probably on positive ions). The coagulation of small clusters to form larger aerosols is also likely in the free air and thus a part of radon daughters activity is likely to be distributed on water clusters in the submicron size range. The presence of negative charges and humidity can greatly facilitate the formation of cluster aerosols.

In the presence of other aerosol of the same size range as the cluster aerosols, the attachment probability may be expected to be proportional to the population of the aerosol of each type. Thus, by deliberate increase in the concentration of negative ions in humid atmosphere it is possible to increase the population of cluster aerosols to which radon daughters can be attached preferentially.

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ИЗУЧЕНИЕ МЕХАНИЗМА ОБРАЗОВАНИЯ АЭРОЗОЛЕЙ СОДЕРЖАЩИХ ДОЧЕРНИЕ ПРОДУКТЫ РАДОНА

Найдено, что на образование аэрозолей с дочерними продуктами радона заметно влияет наличие зарядов и паров. Эксперементы, проведенные с естественным радоном в воздухе, показали, что дочерние продукты радона ведут себя в сухом профильтрованном воздухе как однозарядные ионы с высокой подвижностью, тогда как при наличии зарядов определенного знака и паров они атакуются группами образовавшихся аэрозолей. В этих эксперементах группы аэрозолей образовывались из паров этилового спирта при наличии маленьких отрицательных заряженных ионов. Знание механизма присоединения дочерных продуктов радона к группам аэрозолей было использовано также для оценки радона образующегося в воздухе.

Радиоактивность этих аэрозолей изучалась фильтрованием через мембранные фильтры. Степень равновесия между радоном и продуктами его распада в атмосферном воздухе была изучена на основе этого же механизма. Этот механизм имеет фундаментальное значение для понимания природы дочерних продуктов радона при различных условиях в окружающей среде.