■ 論　　文 ■

Formation of Ultrafine Particle by the Polonium-218 Ions under Different Humidity Conditions

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ABSTRACT

A number of investigators have reported the formation of the radiolytic ultrafine particles produced by the interaction of ionizing radiation with water vapor. Previous studies have suggested that a very high localized concentration of the OH radical produced by the radiolysis of water can react with trace gas like organic vapors and produce lower vapor pressure compounds that can then nucleate. In order to determine water vapor dependence of the active, positively charged, first radon daughter(Po-218), an experiment was conducted using a well-controlled radon chamber. The activity size distribution of the radon daughter in the range of 0.5-100 nm was measured using the parallel graded wire screens system. Measurements were taken for different relative humidity. The resultant activity size distributions were analyzed. The addition of water vapor to the radon carrier gases resulted in the formation of ultrafine particles by OH radicals formed by radon radiolysis. It may be due to the neutralization of charged Po-218 ion with water vapor through the radiolysis.

Key words : *radon daughter, Po-218, radon chamber, parallel graded wire screen system, radiolysis.*

INTRODUCTION

In the past, studies related to radon were focussed on uranium miners and homes built with contaminated materials. Now, following increased measurement efforts, radon in indoor air has become a public health concern. The concern is being increased among the public that indoor radon and radon daughters represent a significant threat to public health. However, there are still many uncertainties as to the fundamental chemical and physical characteristics of the radon daughters.

Radon itself is an inert gas. However, its daughters are chemically active. Radon-222, having a half-life of 3.823 days, decays into a series of radioactive daughters, polonium

-218(RaA, $t_{1/2}$=3.11 min), lead-214(RaB, $t_{1/2}$=19.8 min), bismuth-214(RaC, $t_{1/2}$=26.8 min) and polonium-214 (RaC', $t_{1/2}$=162μs), that emit 2 alpha and 2 beta particles in their decay to long-lived lead-210(RaD, $t_{1/2}$=22.3 years).

The inhalation of these radon daughters can lead to the deposition of radioactive particles on the surface of tracheo-bronchial tree. Subsequent radioactive decay can deliver a significant dose to the respiratory system. Particle deposition in the tracheo -bronchial tree is a function of the size of the particles and the flow characteristics in the various dimensions of the airways[1]. Thus, the determination of the activity size distribution of the ultrafine(0.5-5 nm) and larger size particles associated with the radon daughters is needed.

When the radon daughters are formed in air, they rapidly attached to existing aerosol particles[2]. This attachment give rise to the existence of so-called attached and unattached fractions, where the latter has traditionally been assumed to consist of free atoms of the size of the polonium atom. The distinction originates from the inability of particle detection instruments to detect particle under 5 nm in diameter. Researchers have attempted to separate attached and unattached fractions using the concept that the unattached fraction has a single, constant diffusion coefficient. The concept has lead to reported "unattached" fraction ranging from 0-20%. Lung deposition models also have incorporated the "unattached" fraction concept[3]. However, with recognition of the true nature of the "unattached" fraction, it is now evident that current aerosol techniques do not permit the distinction of the "unattached" and "attached" fraction[4].

In this study, ultrafine particles generated by radon radiolysis are detected by observing the radon daughter activity associated with them following their formation. Ultrafine particle activity size distributions were generated inside radon chamber using water vapor and no trace gas. Non-conventional, a parallel graded wire screen system was used to determine the acitivity size distributions[2]. The wire screen penetration theory proposed by Cheng et al.[5] was used to determine the penetration characteristics of the screen stages. Semi-empirical correction to the 0.5-2 nm size range has been obtained from kinetic theory[2]. The wire screen diffusion battery stage data were deconvoluted using Twomey[6] algorithms to yield activity size distribution information.

THEORETICAL CONSIDERATIONS

A parallel graded wire screen system was built from a 25 mm in-line gas filter assembly for the study. The wire screen system consists of five graded wire screen samplers. Each wire screen sampler has a series of single wire screens mounted on brass rings with the wire mesh number increasing in the direction of the flow. The wire screen penetration theory proposed by Chen and Yeh[7] has been used to determine the penetration characteristics for the wire screen stages. The penetration fraction for a single wire screen stage with wire Reynold number Re_f < 1 and ultrafine parti-

cles, d < 0.1 mm in diameter, is given by

$$P = 1 - \eta = \exp\left[-\frac{(4)(2.7)}{\pi}(WVP)^{\frac{2}{3}}(D)^{\frac{2}{3}}\right]$$

$$(1)$$

where $\quad WVP = U(WF)^{1.5} \qquad (2)$

is the wire velocity parameter in cm^2/s,

$$WF = \alpha \ w/(1-\alpha)/d_f^{5/3} \qquad (3)$$

is the wire factor in $cm^{-2/3}$ and

$$\alpha = (m_A/\rho_f)/(A \ w) \qquad (4)$$

is the soild volume fraction in demensionless.

In Equations (1)-(4), η is collection efficiency, d_f is the wire diameter, w is the wire screen thickness, U is the flow velocity and D is the particle diffusion coefficient, m_A is the mass of a screen of area, A, and ρ_f is the density of the screen material. Equation (1) has been obtained using the fan model filtration theory constant, B=2.7, as suggested and verified by Cheng and Yeh[7] for d > 15 nm and Scheibel and Porstendorfer[8] for d > 4 nm.

In the ultrafine particle range where diffusional collection predominates, Equation (1) determines the particle penertration through a wire screen. The evaluation of the particle size versus penetration characteristics from the equation requires the knowledge of the relationship between particle size and diffusion coefficient. The expression for the diffusion coefficient of an aerosol particle derived from Stokes' law is given by :

$$D = kTC/3\pi\mu d, \qquad (5)$$

where k is the Boltzmann constant, T is the temperature in Kelvin, μ is the viscosity of air, d is the particle diameter and C is the Cunningham slip correcton factor given by Friedlander[9] as,

$$C = 1 + \lambda/d\{2.514 + 0.8 \ \exp(-0.55 \ d/\lambda\}, \qquad (6)$$

where λ is the mean free path of the gas. The original slip correction factor derived by Cunningham[10] is $C = 1 + 2.52\lambda/d$ and its use extends the range of Stokes' law to below 0.01 mm[11]. Equations (5) and (6), however, overestimate the diffusion coefficient in the 0.5-1.75 nm molecular cluster size range.

For molecular clusters of 0.5-2 nm in diameter, kinetic theory can be used to determine the diffusion coefficient of the cluster[12,13]. An expression for the diffusion coefficient of a cluster, D, was derived by Loeb from kinetic theory considering two-body elastic collisions between the clusters and the gas molecules, and is given by :

$$D = \frac{0.815V_r\{(M+m)/M\}^{1/2}}{3\pi s^2 N} \qquad (7)$$

where V_r is the root mean square velocity of the gas, N is the number concentration of gas molecules, s is the sum of the radii of the gas molecules and of the cluster, M is the molecular weight of the cluster and m is the molecular weight of the gas.

The diffusion coefficient of a charged cluster can be significantly different from that of an uncharged cluster of the same physical size and mass, especially for small

cluster sizes. Chapman and Cowling[14] have used a model developed by Sutherland [15] to derive a relation for the diffusion coefficient of charged clusters, as discussed by Porstendorfer[16], and is given by :

$$D = \frac{0.815V_r\{M+m)/M\}^{1/2}}{3\pi s^2 N\{1+0.402e^2 a^3/4s^4 kT\}} \quad (8)$$

where a is the air molecule collision radius and e is the elementary charge. A comparison between the Stokes-Cunningham equations(5)-(6) and the equations (7)-(8) for uncharged and charged(+1 charge) clusters in the 0.5-2 nm size range, which are plotted without the mass factor$\{M+m)/M\}^{1/2}$, is presented in Fig. 1.

For wire screen diffusion battery analysis which results in description in terms of a particle size spectrum, the equations (7)-(8) from kinetic theory in the 0.5-2 nm size range and the corrected Stokes-Cunningham equations (5)-(6) in the 2-100 nm size range were used. The wire screen penetration equation (1), combined with equations (5)-(8) for the particle diffusivity, allows the determination of the penetration characteristics of the various wire screen stage over the diffusion coefficient spectrum of interest.

EXPERIMENTAL MEASUREMENT

A schematic diagram of the experimental set-up used to generate ultrafine particles in the radon chamber is shown in Fig. 2. The radon chamber was operated using purified, compressed air mixed with radon and water vapor. Compressed air was passed through
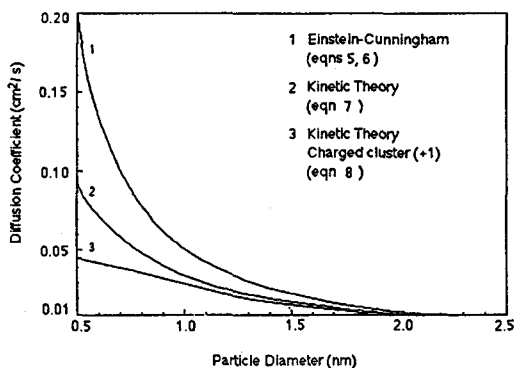

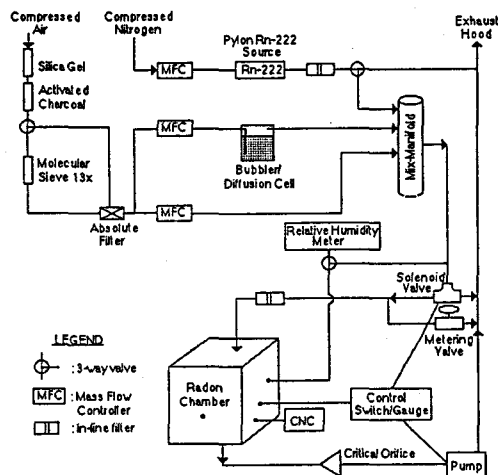Fig. 1. **Diffusion coefficient in the 0.5-2.5nm size range.**

Fig. 2. **The layout of the radon chamber.**

an air purification system consisting of silica gel, activated charcoal, molecular sieve, and $0.2\,\mu m$ pleated membrane filters. Mass flow controllers were used to meter accurately and maintain the required air flows in the system. The radon chamber was fabricated of edge-welded 0.4 mm thick stainless steel, yielding dimensions of 180 cm $\times 120$ cm$\times 120$ cm(approximately 2.5 m^3).
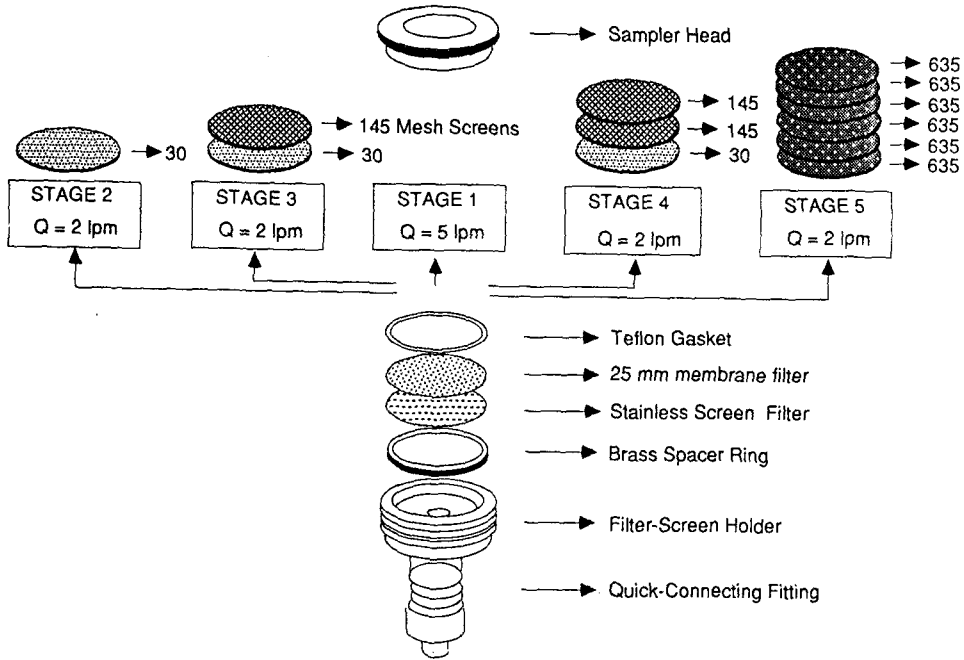
Fig. 3. The diagram of the wire screen system.

Humidification of the air stream was accomplished through the use of two bubblers immersed in a constant temperature water bath. The humidity level of the chamber was monitored using a dew-point hygrometer. The radon-laden nitrogen was mixed with the compressed air to obtain a radon concentration of 2.78×10^4 Bq/m³ for an air flow rate of 1.9×10^4 cm³/min, resulting in an average chamber residence time of 126 minutes. Radon is generated by a dry, flow-through 1025 kBq and 850 kBq Ra-226 sources (Pylon Model RN-1025) using a mass flow controlled rate of 100 cm³/min. The temperature and humidity inside the chamber are continuously record-ed and a TSI Model 3025 Condensation Nuclei Counter(CNC) monitors the detect-able aerosol concentration through a closed -loop sampling system(Fig. 2). The new CNC, having relatively good detection efficiency characteristics(60-70%) for parti-cle diameter below 5 nm, was a useful device for monitoring the detectable particle number concentration levels in the chamber [17]. In these experiments, external aero-sols were not used.

A parallel graded wire screen system used in this study utilizes multiple adapted filter holder samplers with each containing a specific combination of wire screens and a backup filter. The samplers are operated in parallel at specific flow rates(Fig. 3), and after 5 min sampling interval the backup filters are analyzed for collected activity by the Tsivoglou gross alpha method, using the 60 min Nazaroff counting sequence[18]. Extreme care for the samplers design was

taken to minimize wall loss effects for screen combinations with d < 5 nm. This system was used to the study and characterize the activity distribution generated in the radon chamber. Tables 1 and 2 list the screen and operating parameters for the parallel graded wire screen system. A switching valve allows grab samples to be taken through the graded wire screens sampler(Fig 3), which is operated with the sampler head threaded into an adjacent sampling port.

The sampling procedure utilized with the graded wire screens system consisted of a grab sampling period of 5 minutes duration, followed by gross-alpha analysis[19] of the collected activity on the wire screens and filter using ZnS(Ag)-coated mylar scintillator films on an array of photomultiplier tubes(PMT).

RESULTS AND DISCUSSION

Experiments were performed with the radon chamber, with the radon activity maintained at 2.78×10^4 Bq/m³, to permit studies of the formation mechanism of ultrafine particles at low and high humidities. Using equation(6), the particle size represented by Fig. 4 was estimated to be 0.5 nm corresponding to the diffusion coefficient of 0.049 cm²/sec. The use of an activiated charcoal filter to purify the compressed air resulted in a reduction of Po-218 activity in the 1.5-10 nm size range (Fig. 4) that could be ascribed to the removal of trace organics introduced by the laboratory air compressor.
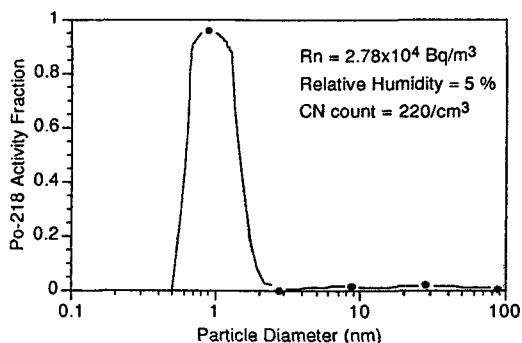
By introducing water vapor into the radon

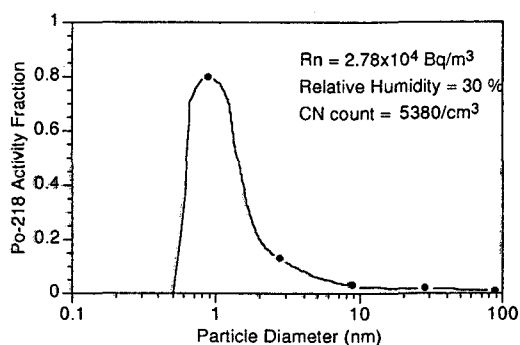Fig. 4. Activity Size Distibution(5% Relative Humidity)

Fig. 5. Activity Size Distibution(30% Relative Humidity)

chamber at 5% relative humidity, ultrafine particles were produced at 30% relative humidity, having a slight increase in the Po-218 activity associated with radiolytic particles 1.5-10 nm diameter(Fig. 5). This activity size distribution curve indicates the existence of a distribution of ultrafine particles. A possible formation mechanism of ultrafine particle is as follows :
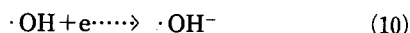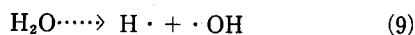
$$H_2O \cdots \cdots > H \cdot + \cdot OH \qquad (9)$$
$$\cdot OH + e \cdots \cdots > \cdot OH^- \qquad (10)$$
$$\cdot OH^- + Po^+ \cdots \cdots > Po + \cdot OH. \qquad (11)$$

Table 1. Screen parameters and maximum air velocity for wire screens used.

Mesh (in⁻¹)	d_f (μm)	w (μm)	α	U_{max} ($Re_f=1$) (cm/s)
30	165.1	349.9	0.145	9.3
100	55.8	122.2	0.161	27.5
145	55.8	163.9	0.176	27.5
400	25.4	72.5	0.208	60.6
635	20.0	50.0	0.345	77.0

Table 2. Screen combinations, operating parameters and stage diameter for parallel graded wire screen system.

Stage No.	Combination Mesh No.	Q (1/min)	V (cm/s)	d (nm)
1	30	2.0	8.6	0.9
2	30*145	2.0	8.6	2.8
3	30*145*635	2.0	8.6	8.8
4	6 Screens of 635	2.0	8.6	28.8

Porstendorfer and Mercer[20] reported that 88% of Po-218 atoms exist as positively charged(+1) ions immediately following recoil from the decay of Rn-222, with the remaining 12% being neutral. The subsequent neutralization of the charged Po-218 ions has been shown to occur by small-ion recombination, electron transfer and electron scavenging mechanism[21]. Fig. 5 shows the Po-218 activity distributions obtained from the addition of water vapor to radon carrier gases in the chamber. The decrease in Po-218 activity in the first interval(0.5-1.5 nm) with increasing water vapor content(Fig. 5) indicates neutralization of charged Po-218 with vapor through the radiolysis mechanism. The neutralization of polonium ions and water vapor in nitrogen could be explained by the electron scavenging mechanism(Equations 10 and 11). Furthermore, the hydroxyl radicals from water vapor radiolysis have been proven to be the electron scavengers that result in the neutralization of polonium ions from water vapor.

The presence of airbone compounds that react with hydroxyl radicals to form higher volatility compounds enhances a change in the size distribution and thus the diffusivity of the ultrafine mode of the polonium activity size distribution. More detailed studies of the mechanism and its dependence on reactant and water vapor concentration are required. The presence of airborne compounds that react with hydroxyl radicals to form a condensable compound could form molecular clusters with water molecules. These embryonic clusters could grow and cause ultrafine particle formation.

Only background condensation nuclei (1-300/cm³) were detected when no trace gas was injected into the radon chamber at low humidity(Fig. 4). However, a larger number of concentration nuclei were formed at 30% relative humidity(Fig. 5). Increasing amounts of water vapor led to increased CNC reading. And the increase of CNC reading may be due to the formation of ultrafine particle by the introduction of water vapor at low humidity.

SUMMARY AND CONCULSIONS

The formation of ultrafine particles (d > 0.

5 nm) through radon radiolysis has been studied by determining the Po-218 activity size distributions in the diffusion coefficient range, 0.049-6.75×10^{-6} cm²/sec, following the addition of water vapor to pure gas atmospheres. A new-born Po-218 ion produced under low humidity condition (5% relative humidity) was estimated to be the particle of 0.5 nm corresponding to the diffusion coefficient of 0.049 cm²/sec.

The addition of water vapor to the radon carrier gases resulted in the formation of ultrafine particles by OH radicals formed by radon radiolysis. The ultrafine particles formed in the recoil path of the Po-218 nucleus were detected by their association with radioactive Po/PoO_2. It may be due to the neutralization of charged Po-218 ion with water vapor through the radiolysis. The neutralization of Po-218 ions and water vapor in nitrogen could be explained by the electron scavenging mechanism. Under the condition where ultrafine particle formations was observed, Po-218 ions were found to be associated with particles less than 10 nm in diameter.

CNCs used by earlier studies suffer from rapidly decreasing detection efficiencies in this range[22, 23]. When CNCs with conventional particle detection system are used, the contribution of ultrafine particle (0.5-5 nm) to lung alpha dose should be made carefully for exact dose estimation.

Further studies for the effects of the addition of organic vapors and SO_x on particle formation will be investigated and direct measurements of the charged Po-218 fraction will be included.

RRFERENCES

1. T.L. Chan and M. Lippmann, "Experimental Measurements and Empirical Modeling of the Regional Deposition of Inhaled Particles in Humans." *Amer. Ind. Hyg. Assoc. J.* **41**, 399(1980).

2. R.F. Holub and E.O. Knutson, "Radon and its Decay Products : Occurrence, Properties and Health Effects.", Washington D.C., American Chemical Society, (1987).

3. A.C. Chamberlain and E.D. Dyson, "The Dose to the Trachea and Bronchii from the Decay Products of Radon and Thoron." *Brit. J. Radiol.* **29**, 359(1956).

4. M. Ramamurthi and P.K. Hopke, "On Improving the Validity of Wire Screen Unattached Fraction Radon Daughter Measurements." *Health Phys.* **56**, 189(1989).

5. Y.S. Cheng, J.A. Keating and G.M. Kanapilly, "Theory and Calibration of a Screen-type Diffusion Battery." *J. Aerosol Sci.* **11**, 549(1980).

6. S. Twomey, "Comparison of Constrained Linear Inversion and an Iterative Nonlinear Algorithm Applied to the Indirect Estimation of the Particle Size Distribution." *J. Comput. Phys.* **18**, 188(1975).

7. Y.S. Cheng and H.C. Yeh, "Theory of Screen Type Diffusion Battery." *J. Aerosol Sci.* **11**, 313(1980).

8. H.G. Scheibel and J. Porstendofer, "Penetration Measurement in the Ultrafine Particle Size Range." *J. Aerosol Sci.* **15**, 549(1986).

9. S.K. Fridlander, *Smoke, Dust and Haze*, New York, John Wiley & Sons, Inc. (1977).

10. M.E. Cunningham, "On the Velocity of Steady Fall of Spherical Particles through Fluid Medium." *Proc. Roy Soc.* **83A**, 365 (1910).

11. C.N. Davies, "Definitive Equations for the Fluid Resistance of Spheres." *Proc. Phys. Soc.*, **57**, 259 (1945).

12. L.B. Loeb, *The Kinetic Theory of Gases*, 3rd Ed., Dover Publications, New York, 554 (1961).

13. O.G. Raabe, "Concerning the Interactions That Occur between Radon Decay Products and Aerosols." *Health Phys.* **17**, 177 (1969).

14. S. Chapmann and T.G. Cowling, *The Mathematical Theory of Non-uniform gases*, Cambridge University Press, Cambridge, England (1958).

15. B. Sutherland, "Molecular Diameter." *Phil. Mag.* **19**, 25 (1910).

16. J. Porstendofer, "Die Diffusioneffizienten und Mittleren Freien Weglangen der Geladenen und Neutral Radon-folge Produkte in Luft." *Zeitschift fur Physik* **213**, 384 (1968).

17. P.B. Keady, V.L. Denier, G.J. Sem and M.R. Stolzenburg, "Condensation Nucleus Counter Designed for Ultrafine Particle Detection above 3 nm diameter", Paper presented at the 12th International Conference on Atmospheric Aerosols and Nucleation, 22-27 August, Vienna, Austria (1988).

18. W.W. Nazaroff, "Optimizing the Total -alpha Tree-count Technique for Measuring Concentrations of Radon Progeny in Residences." *Health Phy.* **44**, 387 (1984).

19. J.W. Thomas, "Measurments of Radon Daughters in Air." *Health Phys.* **23**, 783 (1972).

20. J. Porstendofer and T.T. Mercer, "Influence of Electric Charge and Humidity upon the Diffusion Coefficient of Radon Decay Product." *Health Phy.* **15**, 19 (1979).

21. G. Frey, P.K. Hopke and J.J. Stukel, "Effects of Trace Gas and Water Vapor on the Diffusion Coefficient of Polonium -218." *Science* **211**, 480 (1981).

22. J.W. Agrawal and G.J. Sem, "Continuous Flow, Single-Particle Counting Condensation Nuclei Counter." *J. Aerosol Sci.* **11**, 343 (1980).

23. H. Bartz, H. Fissan, C. Helsper, Y. Kousaka, N. Fukushima, P.B. Keady, S. Kerrigan, S.A. Fruin, P.H. McMurry, P.H. Pui and M.R. Stolzenburg, "Response Characterstics for Four Different Condensation Nuclei Counters to Particles in the 3-50 nm diameter range." *J. Aersol Sci.* **5**, 443 (1985).

다른 습도조건하에서 Po-218 이온들의 극소입자형성에 관한 연구

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요　　약

물분자와 전리방사선과의 상호작용에 의하여 생성된 방사능극소입자에 관한 많은 연구결과가 보고되어 왔으며, 특히 이전 연구에서는 물분자의 방사성분해에 의해 발생한 수산화라디칼의 높은 농도는, 유기물기체와 같은 실내기체와 반응즉시 낮은 증기압의 화학물로 변하여 극소입자가 된다고 알려져 왔다. 본 연구에서는, 라돈의 첫째딸핵종인 Po-218에 대한 물분자와의 의존성을 조사할 목적으로, 실내기체의 최적제어가 가능한 라돈챔버를 사용하여 일련의 실험들을 수행하였다. 특별히 설계 제작된 평행등급 금속망필터시스탬을 사용하여, 서로 다른 습도조건하에서 0.5-100 nm 크기의 라돈딸핵종에 대한 방사능크기분포도가 얻어졌으며, 그 결과가 분석되었다. 라돈가스챔버내에 수증기분자의 첨가와 동 수증기분자의 방사성분해에 의하여 생성된 수산화라디칼에 의한 극소입자들의 형성을 확인하였는데 이는 수증기의 방사성분해과정에서 Po-218이온과 수증기분자 사이에 중화과정 때문인 것으로 밝혀졌다.

Key words : 라돈딸핵종, Po-218, 라돈챔버, 평행등급 금속망필터시스템, 방사성분해