■ 論　文 ■

A Kinetics Study of Rn Daughter and Atmospheric Trace Gas Using AIpha Track Detection

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알파비적검출방법에 의한 대기중 라돈딸핵종의 화학적 동특성연구

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Abstract — A number of investigators have reported formation of radiolytic ultrafine particles produced by the interaction of ionizing radiation with atmospheric trace gases. Previous studies have suggested that a very high localized concentration of the hydroxyl radical produced by the radiolysis of water can react with atmospheric trace gases such as SO_2 and produce lower vapor pressure compounds that can subsequently nucleate. To determine the trace gas and water vapor concentration dependence of the active, positively charged, first decayt product of radon (Po-218), a well-controlled radon chamber was used in this research. The mobility spectrum of the decay products in the range of 0.07-5.0cm²/V.sec from the radon chamber was measured using alpha track detector installed inside a specially-designed electrostatic spectrometer. Measurements were taken for different concentrations (0.5ppm to 5ppm) of SO_2 in purified, compressed air. A kinetics study following the clustering of SO_2 around the PoO_x^+ ion in an excess of SO_2 for interpretation of the reaction processes was performed.

   Key words: radiolytic ultrafine, particle, radiolysis, radon chamber, mobility spectrum.

요약 — 과거 물분자와 전리방사선과의 상호작용에 의하여 생성된 방사능 극소입자에 관한 많은 연구결과가 보고 되어 왔다. 특히 최근연구에서는 물분자의 방사성분해에 의해 발생한 높은 농도의 수산화래디칼은 실내의 유기가스와 반응후 저증기압의 화합물로 변하여 극소입자를 형성한다고 알려져왔다. 본 연구에서는 라돈의 첫째딸핵종인 Po-218에 대한 대기가스와 물분자와의 상호의존성을 조사할 목적으로, 실내가스의 최적제어가 가능한 라돈챔버를 사용하여 일련의 실험을 수행하였다. 제작된 정전기분광계를 사용하여 라돈의 첫째딸핵종인 Po-218이온에 대해 0.07-5.0cm²/V.sec 범위의 이동도스펙트럼을 측정하였으며, 대기가스로 0.5ppm에서 5ppm까지의 SO_2가스를 사용하여 실험결과를 분석하였다. 라돈챔버내에 물분자의 첨가와 동 물분자의 방사성분해에 의하여 생성된 수산화래디칼에 의한 극소입자들의 형성과정을 확인하였으며 PoO_x^+ 이온 주변에 SO_2가스가 부착하면서 일어나는 화학반응에 대한 화학적 동특성연구를 수행하였다.

   요약 : *방사성극소입자, 방사성분해, 라돈챔버, 이동도스펙트럼.*

INTRODUCTION

Since Polonium-218 (Po-218) is formed from radon decay, its chemistry is very important to understanding the behavior of the radon daughters in indoor air. Po-218 has been chosen here for investigation because it has a long enough half-life to permit atmospheric studies to be done. The Po-218 nucleus has a recoil energy of 110keV and is found to be a singly charged positive ion 88% of the time[1,2]. The neutral species occurs the remaining 12% of the time.

Studies have shown that the presence of trace amounts of contaminants in the carrier gas can lead to formation of ultrafine particles in the gas through radiolysis[3,4]. The ionizing radiation associated with the radon decay can form low vapor pressure compoun-

ds from gas constituents, which could lead to clustering and subsequent growth to ultrafine particles with which the Po-218 can become associated. Cluster and particle formation at smaller sizes in the presence of radon have been shown experimentally[5,6].

The purpose of the research reported here was to take advantage of chemical kinetics of reaction processes to infer the nature of the charged clustering particles formed by radiolysis and its dependence on trace gas. For this purpose, an electrostatic spectrometer capable of measuring the number of the small Po-218 ions in well-defined carrier gases by alpha track detection method was developed [7]. The mobility spectrum of the decay products in the range of 0.07-5.0cm²/V.sec from the radon chamber was measured using alpha track detectors installed inside the sp-
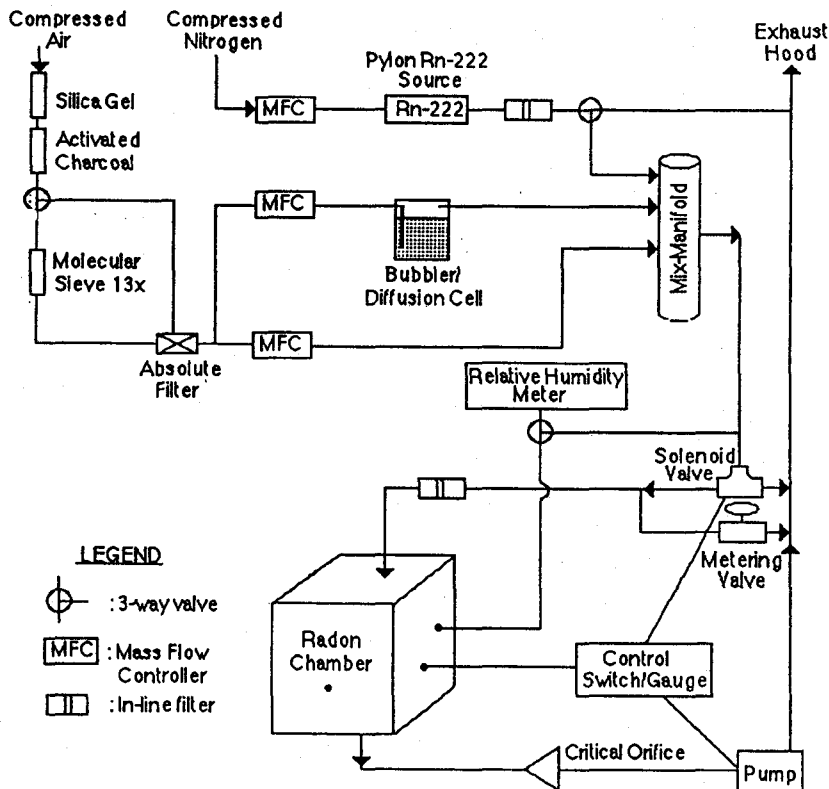

Fig. 1. The layout of radon chamber system.

ecially-designed electrostatic spectrometer [8]. Measurements were taken for different concentrations of SO_2 in purified air. A kinetics study following the clustering of SO_2 around the PoO_x^+ ion in an excess of SO_2 for interpretation of the reaction processes was performed.

EXPERIMENTAL METHOD

In most of the past ion mobility spectrum studies, ambient laboratory air of unknown impurity and humidity levels was used. It was evident that radiolysis was giving rise to cluster formation but the nature of the clustering molecules could not be inferred from the results. Therefore, there was a need for a well-controlled system. For the purposes of this study, the radon chamber as shown in the Fig. 1 was used. Three sets of experiments were conducted using a SO_2 trace gas ranging from o.5 ppm to 5 ppm in same humidity level(5.5% RH) with the radon chamber.
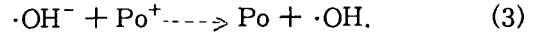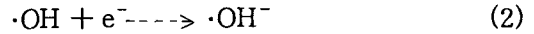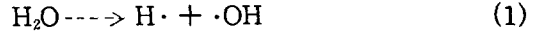
The radon-laden nitrogen was mixed with the compressed air to obtain a radon concentration of 25.9 Bq/1 for an air flow rate of 19 1/min. The SO_2 trace gas, ranging from 0.5 ppm to 5 ppm, was mixed with the radon-aerosol flow using additional mass flow controllers.

After each experiment during sampling time (240min), alpha track film (LR-113 II) was removed from the specially-designed electrostatic spectrometer[8]. And the alpha particles emitted by the Po-218 atoms formed alpha tracks in the film which subsequently were enlarged to visible sizes by an electrochemical etching technique. A $10\mu m$ thick aluminium foil absorber on the film was chosen for the detection of Po-218 atoms[9].
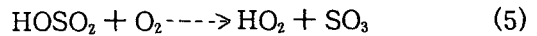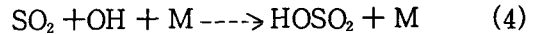
RESULTS AND DISCUSSION

Experiments were performed with the radon chamber, with the radon activity mai-

ntained at 25.9 Bq/1, to permit a kinetics study of the reaction precesses at low humidity level. Water vapor by itself can produce neutralization:

$$H_2O \dashrightarrow H\cdot + \cdot OH \qquad (1)$$
$$\cdot OH + e^- \dashrightarrow \cdot OH^- \qquad (2)$$
$$\cdot OH^- + Po^+ \dashrightarrow Po + \cdot OH. \qquad (3)$$

With the addition of SO_2 at low humidity, several things happen. First, the hydroxyl radicals will oxidize the SO_2 to H_2SO_4 as shown by[10]:

$$SO_2 + OH + M \dashrightarrow HOSO_2 + M \qquad (4)$$
$$HOSO_2 + O_2 \dashrightarrow HO_2 + SO_3 \qquad (5)$$
$$SO_3 + H_2O \dashrightarrow H_2SO_4 \qquad (6)$$

where M is the third body. Second, by the substiution of SO_2 for H_2O in the ion cluster

$$Po(H_2O)_x^+ + y\,SO_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Po(H_2O)_{x-y}(SO_2)_y^+ + yH_2O \qquad (7)$$
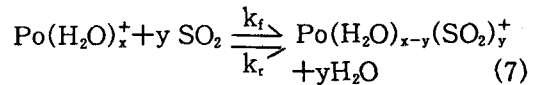
which summarizes the possiblity of the substitution of multiple water molecules by SO_2.

In this research, a kinetics study following the clustering of SO_2 around the PoO_x^+ ion in an excess of SO_2 has been performed. The clustering of SO_2 around the PoO_x^+ ion follows in the presence of excess SO_2. If the concentration of the $[Po(H_2O)_x^+]$ remains constant with time, then the rates of formation and loss are equal. These rates can be written from reaction (7).
Thus

$$d[Po(H_2O)_x^+]/dt = 0 = -k_f[Po(H_2O)_x^+][SO_2]^y + k_r[Po(H_2O)_{x-y}(SO_2)_y][H_2O]^y \qquad (8)$$

Defining equilibrium constant, $k_{eq} = k_f/k_r$ and assuming that $y=1$,

$$k_{eq} = [Po(H_2O)_x^+][SO_2]^y / \{[Po(H_2O)_{x-y}$$

$(SO_2)_y][H_2O]^y\}$ (9)

Since the concentration of the water vapor, $[H_2O]$, is a constant, a plot of $[Po(H_2O)_{x-y}(SO_2)_y]$ against $[SO_2]$ should be a straight line with slope given by:

$$[Po(H_2O)_{x-y}(SO_2)_y]=k_t [SO_2], \quad (10)$$

where $k_t=[Po(H_2O)_x^+]/k_{eq}[H_2O]$. A plot of $[Po(H_2O)_{x-y}(SO_2)_y]$ with $[SO_2]$ will be linear, with the slope increasing with polonium ion
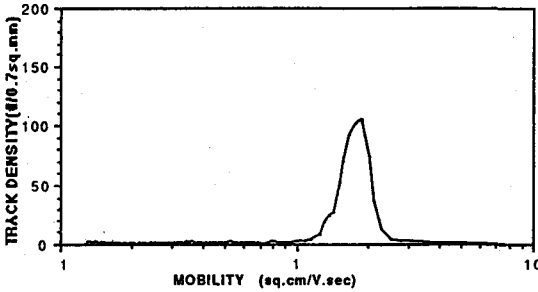

Fig. 4. Ion mobility spectra of Po-218 using radon chamber: 5ppm in SO_2 and 5.5% RH.

Fig. 2. Ion mobility spectra of Po-218 using radon chamber: 0.5ppm in SO_2 and 5.5% RH.

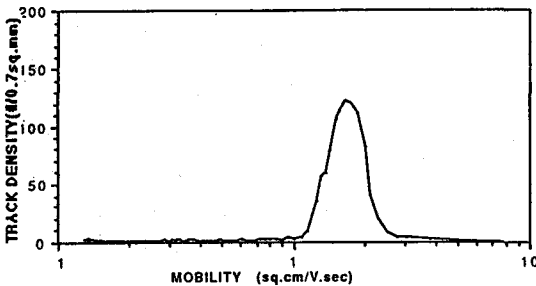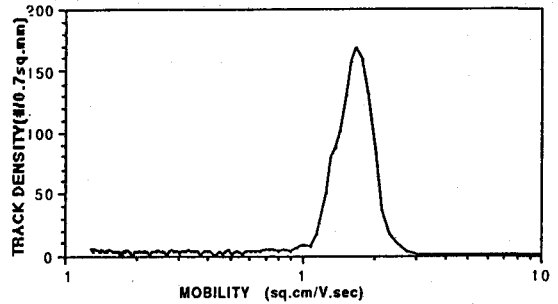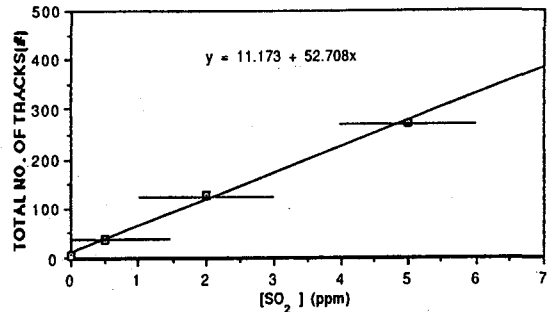Fig. 5. A plot of the total Po-218 ions for sampling time against the concentration of $[SO_2]$.

Fig. 3. Ion mobility spectra of Po-218 using radon chamber: 2ppm in SO_2 and 5.5% RH.

clustering water molecules since k_t depends on $[Po(H_2O)_x^+]$. To see the linearity of the concentrations of $[SO_2]$ and $[Po(H_2O)_{x-y}(SO_2)_y]$ at low humidity, data from Fig. 2 were used.

Since the total number of Po-218 ions having a mobility approximately equal to 1.35 $cm^2/V \cdot sec$ that are deposited for sampling time is proportional to the concentration of $[SO_2]$, a plot of the total number of Po-218 ions deposited versus $[SO_2]$ should be linear. Such a plot is shown in Fig. 5. The total number of Po-218 ions were calculated from a curve fit of the data presented in Figs. 2-4. Fig. 5 shows such a plot of the total ions against $[SO_2]$. As expected, the total number of ions is almost linear with $[SO_2]$. Therefore, the reaction (7) at low humidity dominats. If the $[SO_2]$ is known, the total number of ions at low humidity, I, for $[SO_2]$ concentrations between 0.5-5ppm, may be estimated from the relationship given by:

$$I = 52.7[SO_2] + 11.2. \quad (11)$$

At high humidity, the presence of excess water vapor tends to reduce the number of Po-218 ions. Since the excess water vapor causes greater particle formation rate, there is enough H_2SO_4 being formed for droplets to nucleate and for the clustering to be with this molecule rather than the SO_2. In this case, the reaction(6) is more dominant in increase amounts of water vapor.

CONCLUSIONS

In this research a kinetics study following the clustering of SO_2 around the PoO_x^+ ion in an excess of SO_2 for interpretation of the reaction processes has been performed. Since the concentration of the water vapor, $[H_2O]$, is a contant at low humidty, a plot of $[Po(H_2O)_{x-y}(SO_2)_y]$ with $[SO_2]$ should be linear. To see the linearity of the concentrations of $[SO_2]$ and $[Po(H_2O)_{x-y}(SO_2)_y]$, data obtained at low humidity has been used for this study. If the $[SO_2]$ is known, the total number of ions at low humidity for $[SO_2]$ concentrations between 0.5-5ppm may be estimated from the realtionship given in equation (11) where y is assumed to be 1. It is evident from these results that the reaction process of increasing SO_2 with PoO_x^+ ion (reaction (7)) at low humidity is more dominat than that of a Po-218 ion with hydroxyl radical (reaction (3)).

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