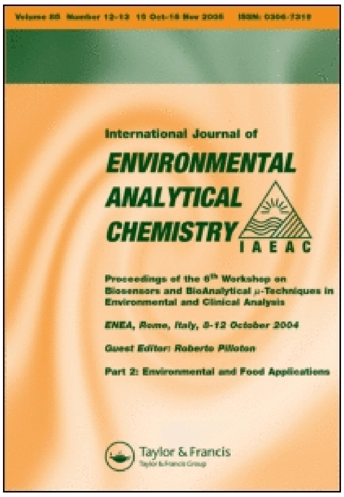

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NITRIC ACID-AIR DIFFUSION COEFFICIENT: EXPERIMENTAL DETERMINATION USING A DIFFUSION CELL

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Trace gaseous nitric acid was generated using a diffusion cell. The determination was made by collection in cellulose filters coated with K_2CO_3 and measuring the concentration by ion chromatography. The measured HNO_3-air diffusion coefficient was $0.0404 \pm 0.0010\ cm^2/s$ (n = 21) for T = 298.15 K and P = 1 atm. Their dependence with the temperature, over the range from 297.15 K to 318.15 K, could be expressed by $D = 10^{-4.7773}.T^{1.366}$ (R^2=0.9467).

KEY WORDS: Nitric acid, diffusion coefficient, diffusion cell.

INTRODUCTION

Nitric acid (HNO_3) is a secondary atmospheric constituent, which is present in the air in the vapour phase[1], and is formed by oxidation of NO_2, by either homogeneous or heterogeneous oxidative mechanisms. Nitric acid is, in some locations, a major contributor to strong acidity in the atmosphere and it is of paramount importance to evaluate the contribution of NOx emissions to rain or fog chemistry and to visibility[1,2]. Indeed, the deposition of nitric acid to the Earth's surface has been associated with ecosystem acidification[3] and particulate ammonium nitrate has been associated with the deterioration of atmospheric visibility[4].

Nitric acid has also been associated to the formation of mutagenic compounds in the atmosphere, like the nitro polycyclic aromatic hydrocarbons (nitro PAHs). Pitts et al.[5] observed the formation of benzo(a)pyrene (BaP) nitroderivatives when BaP was exposed to NO_2 in the presence of nitric acid. Indeed, Tokiwa et al[6] obtained a 150-fold increase in 1-nitropyrene yield when adding ca. 20 ppb of nitric acid to pure air containing 10 ppm of NO_2. Grosjean et al.[7] observed conversion in the order of 99.99% of initial BaP when exposed filters spiked with this compound to nitric acid vapor in pure air. They strongly suggest that nitric acid, rather than NO_2, should be considered in studies of PAH nitration[7].

Usually, nitric acid gas is generated by vaporizing HNO_3 solutions[8] or by passing N_2 over fuming HNO_3[2]. These methods are not convenient to operate over a wide range of concentrations, and to maintain constant vapor concentrations over long operating periods.

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* corresponding author.

The diffusion cells have been used to produce, continuously, low concentrations of vapors[9,10]. It permits the study of some reactions in gas phase, gas-liquid phase and gas-solid phase which involve compounds that are liquid at room temperature. Also, if the diffusion coefficient of the trace reactive gas in air, and their dependence with the temperature, are known, a "perfect-sink" may be designed to operate as an air sampler to deplete a predictable fraction of the gas[8].

Passive samplers based on Fickian diffusion may be designed to collect trace reactive gases in the presence of particles. A convenient design consists of a stagnant tube with an inert inner wall, an open end, and an end cap whose inner surface is a "perfect-sink" for the trace gas [8, 11]. The average ambient concentration of the reactive trace gas is given by

$$C(O) = (mL)/(AtD) \quad (1)$$

where: $C(O)$ = the average concentration at the open end, $\mu g/m^3$

m = mass of reactive trace gas accumulated by the end cap, μg
L = the axial length of the inert tube, cm
A = tube's cross-sectional area, cm^2
t = sampling duration, s.
D = diffusion coefficient, cm^2/s.

The proper use of this procedure depends on the accurate knowledge of the changes of the diffusion coefficient with relation to air temperature. It has been reported HNO_3-air diffusion coefficient within the range of 0.042 to 0.12 cm^2/s(2, 12-16), depending upon the relative humidity, the vapor generation system and the kind of denuder collection. In this work the nitric acid diffusion coefficient, using a diffusion cell has been determined and the dependence as a function of the temperature has been examined.

EXPERIMENTAL SECTION

Preparation of filters

Cellulose filter circles, 45 mm dia. (whatman #41) were prewashed with distilled, deionized water and dried at 40°C. They were immersed in 5% (w.v.) Na_2CO_3, and after the excess of solution was drained off, it was heated at 40°C to incipient dryness.

Diffusion cell

The diffusion cell (Figure 1) was constructed from Pyrex tubing, 13.27 cm long and 3.98 cm o.d. The diffusion tube, DT, which contains the liquid sample is 14 cm long and 0.33 cm i.d. The average length of diffusion path was 6.22 cm and the flow rate through the diffusion cell was 1.0 l/min. The whole device was immersed in a thermostatted bath. An

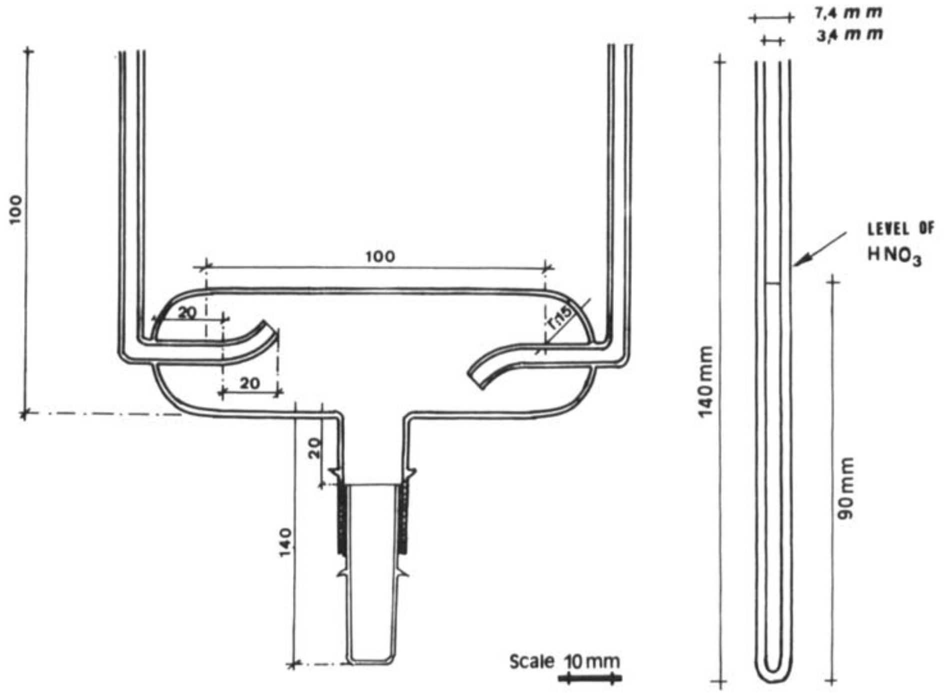

Figure 1 The diffusion cell

overview of the ambient air scrubber, diffusion system and sampling system is shown in Figure 2. Under these conditions the $HNO_3(v)$ concentration delivered (n = 20) was 0,106 ± 0.005 ppmV.

The diffusion rate r (mg/s), can be determined experimentally by quantification of the mass of HNO_3 collected at the sampling system. It permits the determination of the

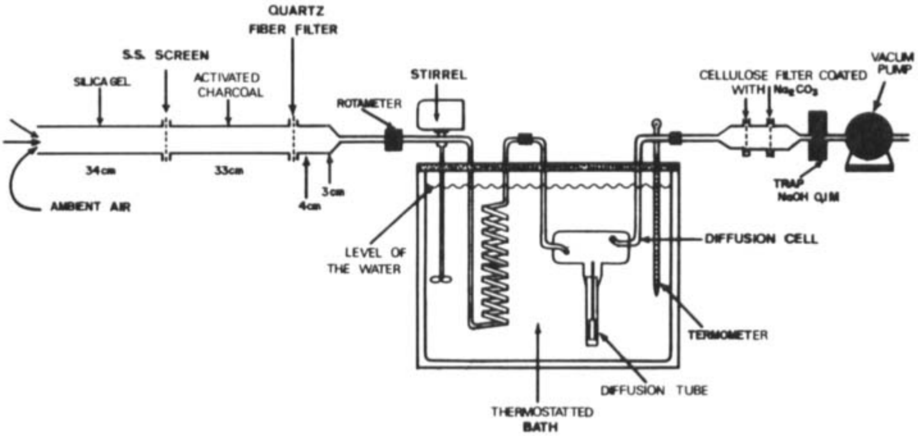

Figure 2 Schematic of the diffusion system

diffusion coefficient D (cm^2/s), from the diffusion equation[9].

$$r = \frac{D.A.M.P}{R.T.l} \ln \frac{P}{P-p} \tag{2}$$

where A = cross sectional area of the diffusion tube, cm^2. M = molecular weight of the nitric acid, g/mol. P = total gas pressure in the diffusion cell, atm. p = partial pressure of vapor at temperature T, atm. R = constant, *l*.atm/mol.K. T = cell temperature, K. *l* = average length of the diffusion path, cm.

Analysis

After sampling, filters were extracted ultrasonically with 25 ml water, during 15 minutes, at room temperature. Nitrate was measured by ion chromatography (Dionex 4000i). The mobile phase was $Na_2CO_3/NaHCO_3$ (0.0031M/0.0039M) at 0.7 ml/min. A more detailed account of analytical procedures can be found elsewere[17].

RESULTS AND DISCUSSION

Collection efficiency of sodium carbonate filters

Initial experiments to evaluate the capacity of sodium carbonate filters were conducted. Varying amounts of HNO_3 were introduced, from the diffusion cell, in two sets, in series, of cellulose filters impregnated with Na_2CO_3. The amount of HNO_3 in the first set of filters were considered as the absorption capacity and when the nitric acid arised the second set of filters it was considered as breakthrough. Results of these experiments were displayed graphically in Figure 3. Absorption capacity of the filters was 15.9 μg HNO_3 before breakthrough occurred.

Nitric acid-air diffusion coefficient

The HNO_3-air diffusion rate (r), measured at the temperature range of 24 – 45°C, and the corresponding diffusion coefficients (D) are shown in Table 1.

Altshuller and Cohen[9] reported that the temperature dependence of the diffusion coefficient is expressed by the equation $D_2/D_1 = (T_2/T_1)^n$, where D_2 and D_1 are the diffusion coefficients at temperatures T_2 and T_1. Application of classical kinetic theory to a model system of rigid spherical molecules leads to a $T^{3/2}$ dependence. The n = 3/2 exponent has been used in several semi empirical equations for diffusion coefficients. Regarding nitric acid the calculated values were 0.113 cm^2/s(2) and 0.122 cm^2/s(12).

In Figure 4 it could be observed the dependence of the nitric acid-air diffusion coefficient

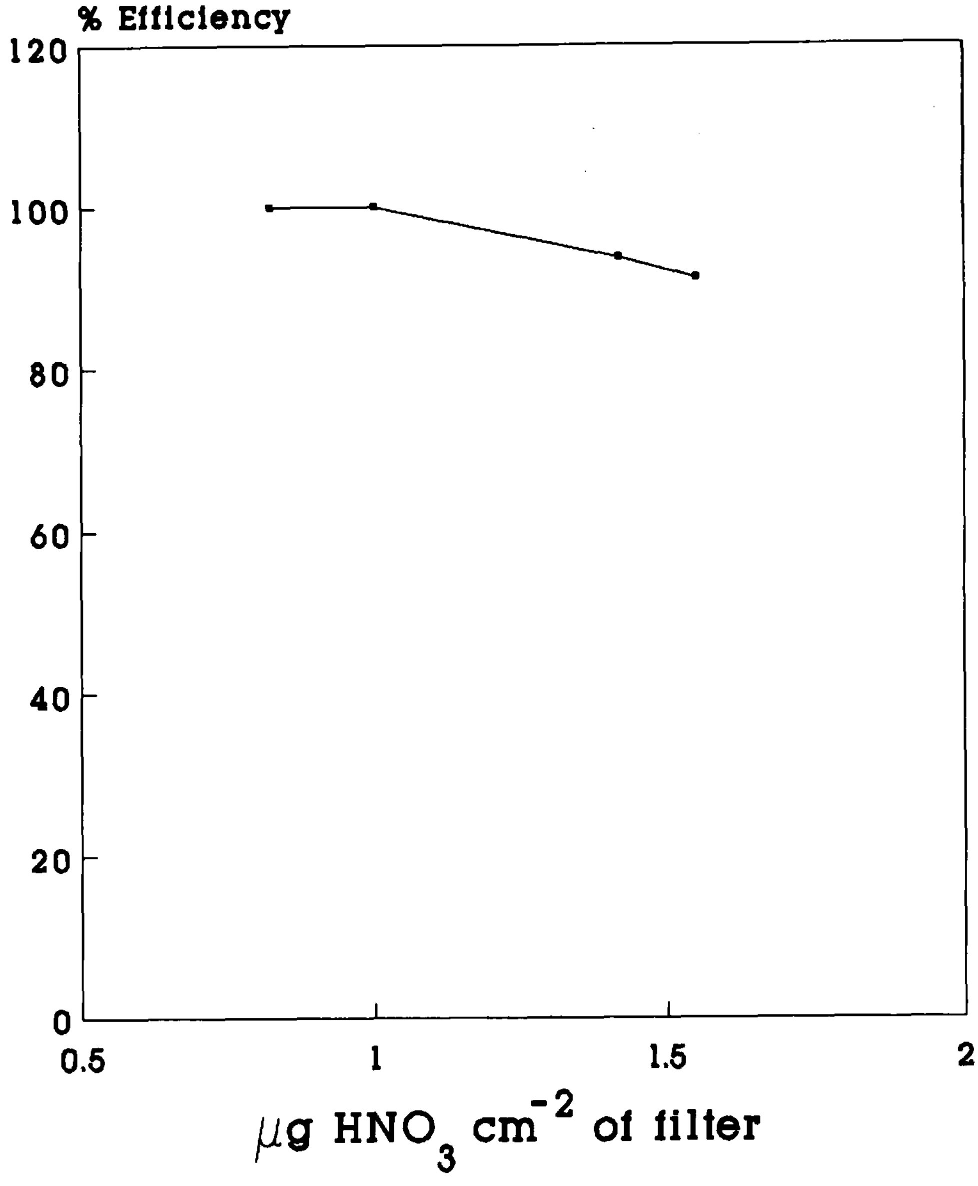

Figure 3 Retention capacity of Na_2CO_3 filters for HNO_3.

with the temperature, in the range of 24°C to 45°C. These dependence can be expressed by the equation:

$$D = 10^{-4.7773}\,T^{1.366} \qquad (R^2=0.9467)$$

the excellent fit indicates that the value for n, determined in this study for the nitric acid vapor, is 1.366.

Table 1 Experimental diffusion rates and diffusion coefficients of HNO_3(v).

Temperature (K)	*Vapor pressure* (atm)*	*Diffusion rate (ng/s)*[a]	*Diffusion coefficient(cm^2/s)*[a]
297.15	0.002865	4.121±0.008	0.0398±0.0001
299.15	0.003250	4.653±0.19	0.0407±0.0017
303.15	0.004171	6.206±0.12	0.0419±0.0007
308.15	0.005605	8.270±0.14	0.0423±0.0007
318.15	0.009934	14.60±0.051	0.0440±0.0015

*from ref. 108
[a]average of four experiments

The weighted values for D to the reference condition T = 298 K and P = 1 atm by

$$D_o = (298/T)^{1.366}D$$

showed $D_o = 0.0404 \pm 0.0010$ cm^2/s (n = 21),.and it agrees well with the value of 0.050 cm^2/s determined by Braman et al.[12] in field studies. However, there are some discrepancies with the value determined by Eatough et al.[2] (0.076 ± 0.020 cm^2/s) using tungstic acid denuders. As well, the value determined in this study does not agree with that obtained in other laboratory studies[2,8], probably due to the vapor nitric acid generation system which used the

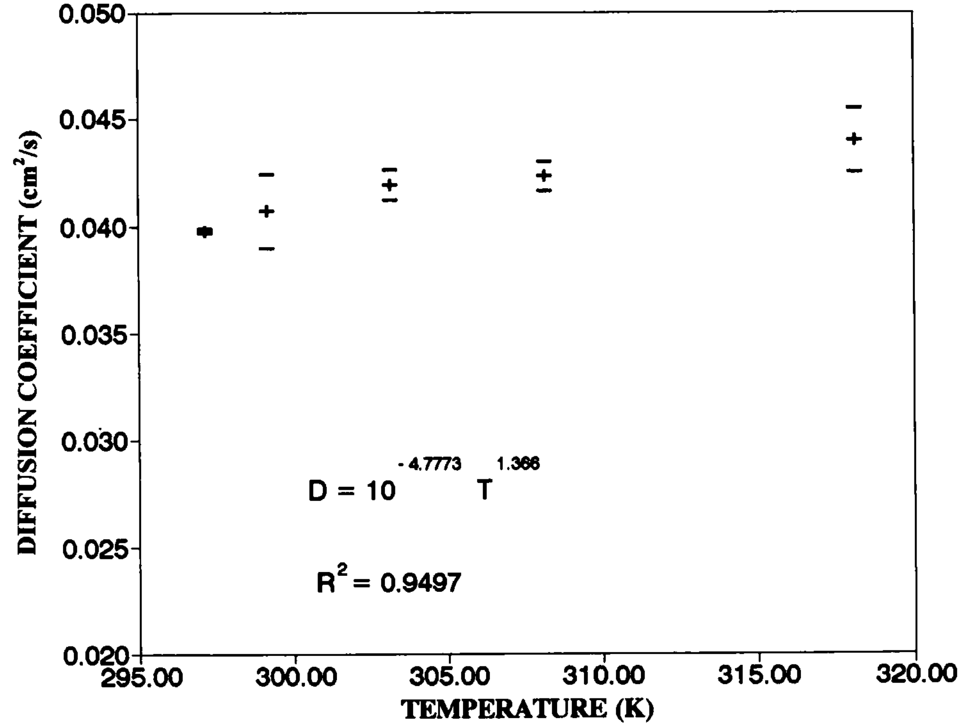

Figure 4 The dependence of the HNO_3 diffusion coefficient with the temperature

vaporizing HNO_3[8] solutions or by passing N_2 over fuming HNO_3[2]. In the system used in this study, the vapor is produced continuously and the diffusion occurs without interference from the carrying stream.

CONCLUSIONS

The diffusion coefficient of HNO_3 in air ($T = 298K$, $P = 1atm$) is $0.0404 \pm 0.0010\ cm^2/s$ ($n = 21$). Their dependence with the temperature can be expressed by the equation $D = 10^{-4.7773} T^{1.366}$ ($R^2 = 0.9467$). It permits the design of a passive sampler for vapor nitric acid, based in the equation 1, where a "perfect-sink" could be a cellulose filter coated with Na_2CO_3 and the collection time depends on the detection limit of the analytical system and the dimensions (A and L) of the sampler.

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