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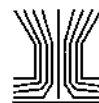
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Design and Testing of a Personal Porous-Metal Denuder

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A personal denuder made of porous-metal disc has been designed and tested. The entire casing and substrate support are made of Teflon, and the sampling flow rate is 2 L/min. The sampler consists of a two-stage cascade impactor (having cut-off aerodynamic diameters of 9.5 and 2.0 μm , respectively) to collect liquid particles and two porous-metal discs (diameter: 2.54 cm; pore size: 100 μm ; thickness: 0.317 cm) to collect basic and acidic gases, respectively. The denuder was tested for gas collection efficiency and capacity at a gas concentration of two times the permissible exposure limit (PEL, promulgated by Taiwan Institute of Occupational Safety and Health (IOSH)), with relative humidity (RH) of $80 \pm 5\%$ and temperature of $30 \pm 3^\circ\text{C}$. The test data indicate that the gas collection efficiency is high, and the capacity is sufficient for the acidic/basic gas sampling in the workplace. Using 5% (w/v, g/mL) sodium carbonate/1% (w/v) glycerol coating on the porous-metal disc, the collection efficiency is $91.2 \pm 0.26\%$ (average \pm standard deviation), $95.08 \pm 0.06\%$ and $100 \pm 0.04\%$, and the capacity is 4.47, 7.2, and 2.5 mg for HNO_3 , HCl and HF, respectively. The collection efficiency for NH_3 for the porous-metal disc with 4% (w/v) citric acid coating is $96.39 \pm 0.13\%$, and the capacity is 33.6 mg.

INTRODUCTION

Diffusion denuder is a sampler for removing gases from an aerosol stream to measure their concentrations separately. Gas or vapor molecules diffuse rapidly to the wall of a diffusion sampler and are adsorbed onto the wall coated with a suitable material. Particles are collected at the downstream filter. The gas concentration can be determined by extracting the coated substrates and analyzing the samples.

Original denuders were made of straight cylindrical tubes (Ferm 1979). Later, Possanzini et al. (1983) designed an annular denuder system with much better gas collection efficiency and absorptive capacity. Pui et al. (1990) designed a compact

coiled denuder with performance comparable to that of an annular denuder. Koutrakis et al. (1993) and Sioutas et al. (1996) developed a glass honeycomb denuder/filter pack system to collect atmospheric gases and particles. The system is considerably smaller than the annular denuder system and can be easily used for large field studies. Wai et al. (1994) developed a high efficiency compact diffusion denuder using porous-metal discs. The small size of the denuder makes it possible to design a compact atmospheric and/or indoor denuder sampling system.

Wai et al. (1994) reported that when using 1% (w/v, g/mL) sodium carbonate/1% (w/v) glycerol coating in the porous-metal disc, the collection efficiencies of SO_2 and HNO_3 were higher than 99% and 93% at 10 L/min, respectively. If a 2% sodium carbonate/1% glycerol coating was used, the gas collection capacity of the porous-metal disc was as high as 8.4 mg for SO_2 . The collection efficiency and capacity have not been determined for other gases. The particle loss in the size range 0.1–2.5 μm for the porous-metal disc was below 3%.

In this study, a personal porous-metal denuder intended for workplace acidic aerosol sampling was designed and tested. The flow rate is 2 L/min. This denuder has a two-stage cascade impactor with the cut-off aerodynamic diameter of 9.5 and 2.0 μm . Two porous-metal discs (diameter: 2.54 cm; pore size: 100 μm ; thickness: 0.317 cm; P/N 1000, Mott Inc., Farmington, CT) were placed downstream of the cascade impactor to remove basic and acidic gases, followed by a 37 mm filter holder to collect particles smaller than 2.0 μm . The cascade impactor was tested for particle collection efficiency and wall loss. The porous-metal discs were tested for gas collection efficiency and capacity of HNO_3 , HCl, HF, and NH_3 at two times the permissible exposure limit (PEL, promulgated by Taiwan IOSH), with a $80 \pm 5\%$ relative humidity (RH) and a $30 \pm 3^\circ\text{C}$ temperature. Currently, the PEL of Taiwan IOSH for HNO_3 , HCl, HF, and NH_3 is 2, 5, 3, and 50 ppm, respectively. The condition at 80% RH and 30°C is a stringent condition and is specified in the standard procedure for certifying a reference sampling and analysis method of the Taiwan IOSH (1996).

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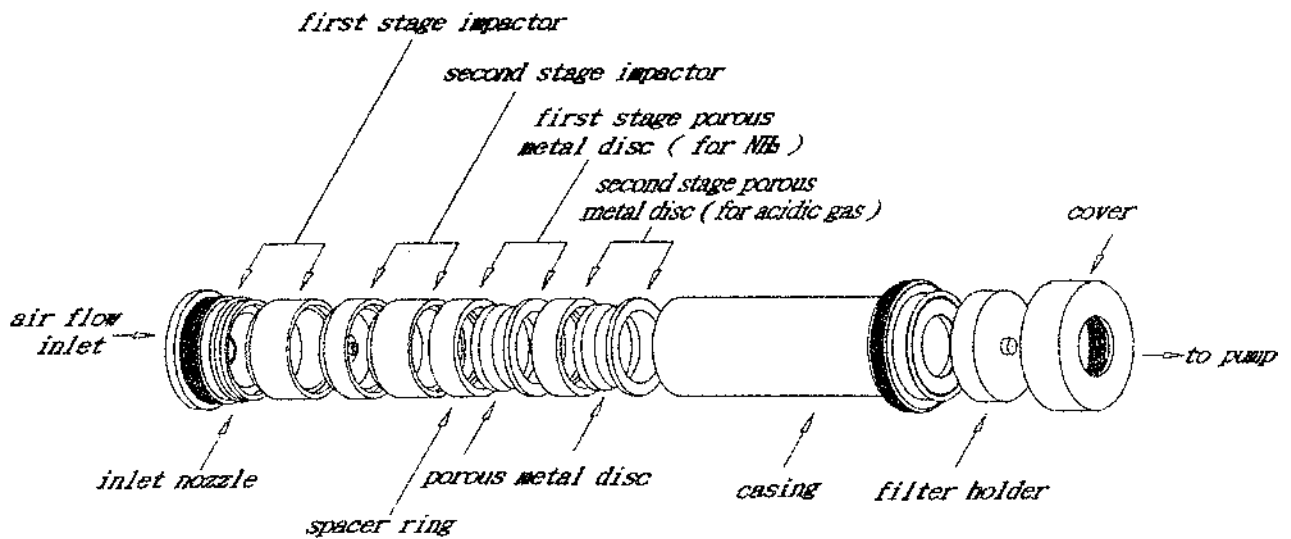


Figure 1. Schematic diagram of the present personal denuder.

PRESENT DESIGN

The schematic diagram of the personal denuder sampler is shown in Figure 1 and its detailed drawing is shown in Figure 2. The sampler is made of Teflon to minimize interaction between internal surfaces and reactive gases. The outside diameter is

34.6 mm, and the total length is 90 mm. The sampling flow rate is 2 L/min.

The cascade impactor is mainly used to remove and classify large liquid particles that may be collected by the downstream porous-metal discs and interfere with gas concentration

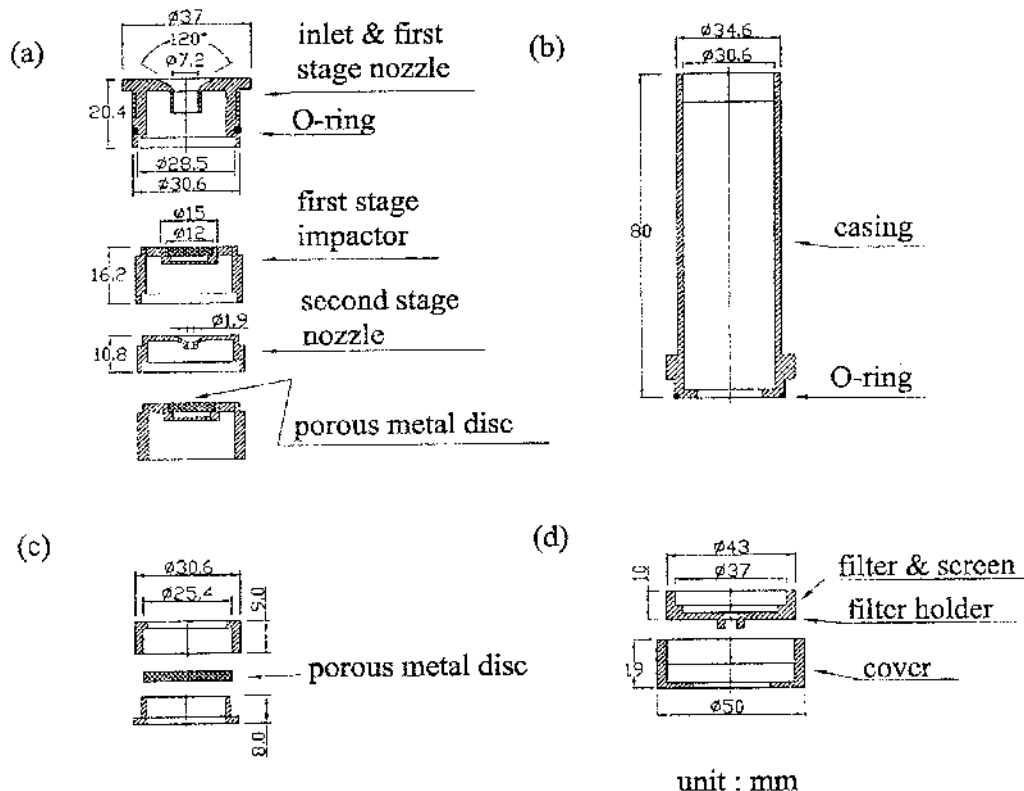


Figure 2. Detailed drawing of the present personal denuder. (a) Cascade impactor, (b) casing, (c) porous-metal disc, and (d) filter holder.

measurement. Liquid particles collected by the cascade impactors can be analyzed further by the ion chromatograph to determine the concentration of particles. Each stage of the cascade impactor has a single round nozzle. The diameter of the nozzle is 7.2 and 1.9 mm for the first and second stage, respectively. Since most of acidic aerosol particles are liquid in the workplace, a removable porous-metal disc (OD: 1.2 cm; other dimensions are the same as PN/1000, Mott Inc.) is used as the impaction substrate to make use of its capillary action to prevent particle overloading problems.

In the loading test, collection characteristics of liquid particles on a flat impaction plate and a porous-metal substrate were compared. Monodisperse oleic acid particles of 10.6 μm in aerodynamic diameter, 5–10 $\#/\text{cm}^3$ in concentration were sampled for 2 h. The total loaded particle mass was about 0.7 mg. The results showed that liquid particle permeated into the porous-metal substrate and no liquid droplets remained on the surface. Therefore the collection efficiency of subsequent particles is not expected to be affected. In comparison, particles pile up into a large liquid droplet on the flat impaction surface, which was subsequently reentrained.

The first and second porous-metal discs were coated with citric acid and sodium carbonate/glycerin to remove ammonia and acidic gases, respectively. Different coating concentrations were tested in order to find a suitable concentration which has a high gas collection efficiency and capacity for 8 h continuous sampling in the workplace. Fine acidic aerosol particles not collected by the impactor and denuder discs are collected by the 37 mm after filter. If volatilization loss of particles from the after filter is a problem, several other filter materials can be used after this filter to absorb volatilized gases. However, volatilization loss is not the objective of this study and was not investigated.

EXPERIMENTAL METHOD

Particle Collection Efficiency and Wall Loss of the Cascade Impactor

The particle collection efficiency and wall loss were determined using monodisperse oleic acid test particles as described in Tsai and Cheng (1995). The particles containing fluorescein dye tracer were generated by a vibrating orifice monodisperse aerosol generator (VOMAG; TSI Model 3450, TSI Inc., St. Paul, MN). The aerosols were dried and the charge neutralized before being introduced into the testing stage of the cascade impactor. After sampling for 5–30 min, the impactor and the after-filter were washed with distilled water buffered with 0.001 N NaOH in known volumes. The washed solution was measured using a fluorometer (10-AU Fluorometer, Turner Designs, CA) to determine the dye concentration of different portions of the impactor and after-filter. Assuming that the dye concentration is proportional to the mass concentration of collected particles, the collection efficiency $\eta(\%)$ and wall loss (%)

can be calculated as follows:

$$\eta(\%) = \frac{M_2}{M_1 + M_2} \times 100\%, \quad [1]$$

$$\text{Loss}(\%) = \frac{M_3}{M_1 + M_2 + M_3} \times 100\%, \quad [2]$$

where M_1 , M_2 , and M_3 are the mass concentration of the after-filter, impactor plate, and the other portions of the impactor, respectively. An aerodynamic particle sizer (APS; TSI Model 3310A) was used to check the monodispersity and steadiness of the testing aerosols before and after each test.

Particle Loss in the Porous-Metal Disc

Particle loss in the porous-metal disc was determined using monodisperse polystyrene latex particles (PSL) generated by an atomizer (Retec X-70/N, Cavetron Corp., Portland, OR) and dried by a silica gel diffusion drier. The PSL particles were further neutralized by a Kr-85 neutralizer before being introduced into a mixing chamber. From the chamber, particles were sampled through the porous-metal disc by a laser aerosol spectrometer (PMS Model LAS-X, Particle Measuring Systems Inc., Boulder, CO) to determine the inlet and outlet particle concentrations (N_1 and N_2). Particle loss in the porous-metal disc, $\text{Loss}_p(\%)$, was calculated as

$$\text{Loss}_p(\%) = \left[1 - \frac{N_2}{N_1} \right] \times 100\%. \quad [3]$$

Gas Collection Efficiency and Capacity of the Porous-Metal Disc

Figure 3 shows the test set up to measure the gas collection efficiency of the porous-metal disc for HNO_3 , HCl , or HF gases. Desirable test gas concentration was generated by aerating clean

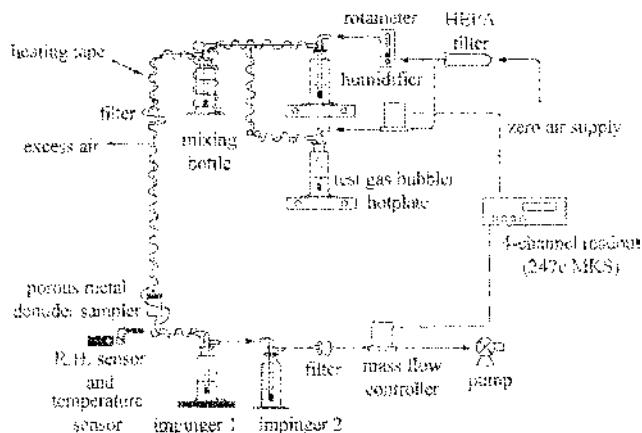


Figure 3. Test set up for measuring gas collection and capacity.

air through a bubbler containing a known concentration of acidic solution. A hot plate was used to heat up the bubbler to facilitate gas generation. To generate NH_3 gas, a standard gas bottle was used instead of a bubbler. The test gas was then mixed in a mixing bottle with humid air coming from a humidifier (also a bubbler) containing deionized water. Heating tape was used throughout the sampling line to prevent gas condensation on the wall. By adjusting the concentration of bubbling liquid, hot plate temperature, and flow rate of the mixing humid air, it was possible to obtain the desirable test gas concentration at two times the PEL, $30 \pm 3^\circ\text{C}$ and $80 \pm 5\%$ RH.

A quartz filter was used to collect small particles that might be generated in the test system before introducing the test gas to the porous-metal disc. Two impingers with proper absorbing solutions were used in series to collect gas that penetrated through the porous-metal disc. After sampling, the porous-metal disc was extracted with distilled deionized water in a low-pressure chamber at 0.2 atm (Wai et al. 1994).

The concentration of the test gas collected on the disc and impingers (M_4 and M_5) was determined by an ion chromatograph (Model 4500i, Dionex Corp., CA). Two impingers were used to collect test gas, and M_5 is the sum of gas concentrations of the two impingers. The second impinger was used to check whether the first one broke through. The gas collection efficiency of porous denuder, $\eta_g(\%)$, was calculated as

$$\eta_g(\%) = \frac{M_4}{M_4 + M_5} \times 100. \quad [4]$$

The gas collection efficiency was measured at the sampling time of 1, 2, 3, and 4 h. At each sampling time, the test was repeated three times to improve the precision of the experiment. Breakthrough time was defined as the time at which the collection efficiency dropped below 95%. Gas collection capacity, expressed in mg, was calculated by the sampling air volume at the breakthrough time multiplied by the test gas concentration.

Two different coating concentrations were used for the test. For acidic gases, 10 ml, 3 or 5% (w/v in g/mL) sodium carbonate, 1% (w/v) glycerol in 1:1 (v/v) methanol/water solution was used. For ammonia gas, 10 ml, 2 or 4% (w/v) citric acid in ethanol was used. The coating solution concentration is higher than that of the denuder used for atmospheric sampling (Wai et al. 1993; Sioutas et al. 1996) since the latter was found to be insufficient for the high challenging gas concentration. After coating, the porous-metal discs were dried by passing nitrogen gas through them.

Careful QA/QC procedure in this study showed that the method detection limit was 1.5, 4.0, 1.5, and 15.1 ppb, in terms of gas phase concentration, for HNO_3 , HCl, HF and NH_3 , respectively, based on 8 h sampling at 2 L/min. The corresponding recovery efficiency from the porous-metal disc for the above 4 gases was 94.7 ± 0.4 , 101.5 ± 1.0 , 103.6 ± 2.2 , and $98.1 \pm 3.8\%$, respectively.

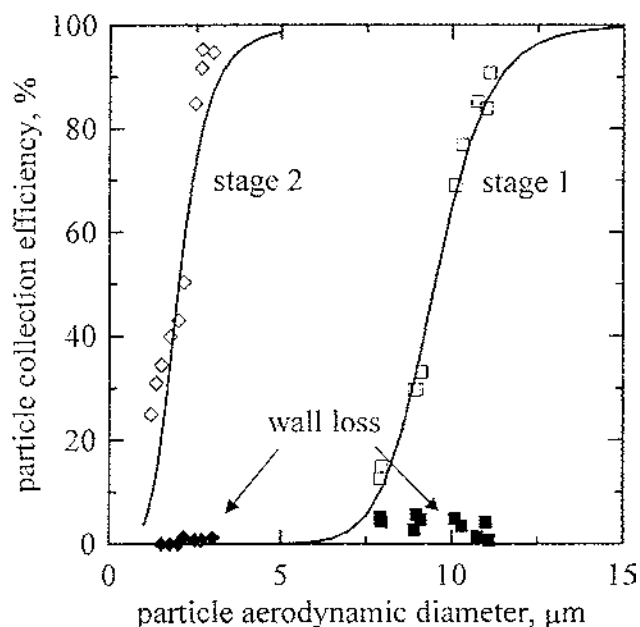


Figure 4. Particle collection efficiency and wall loss of the cascade impactor.

RESULTS AND DISCUSSION

Results from Particle Experiments

Particle collection efficiency and wall loss of the cascade impactor is shown in Figure 4. The cut-off aerodynamic diameter for the first and second stage is 9.5 and 2.0 μm , respectively. The cut-off diameter is smaller than that predicted using Marple's theory (1970), which should be 18.4 and 2.43 μm for the first and second stage, respectively. This is due to partial entrainment

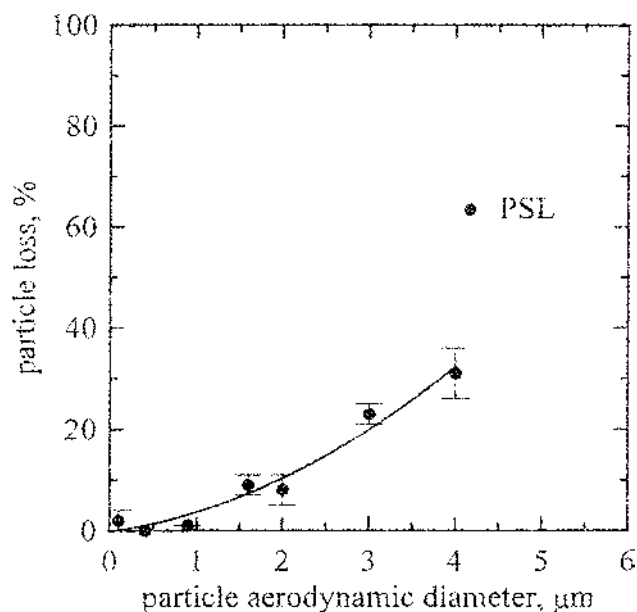


Figure 5. Particle loss in the porous-metal disc.

of the air streamlines into the porous substrate, resulting in additional particle collection. The collection efficiency does not go to zero when the aerodynamic particle diameter approaches zero. In Figure 4, wall loss for the first and second stage of the impactor is shown to $< 5.7\%$ and 1.2% , respectively.

Figure 5 indicates that the maximum particle loss in the porous-metal disc is $< 9\%$ for particle aerodynamic diameters smaller than $2.0 \mu\text{m}$. Loss can be much higher for larger particle sizes. Since particles larger than $2.0 \mu\text{m}$ are removed by the cascade impactor, particles collected in the porous-metal discs are not expected to interfere with gas concentration measurements.

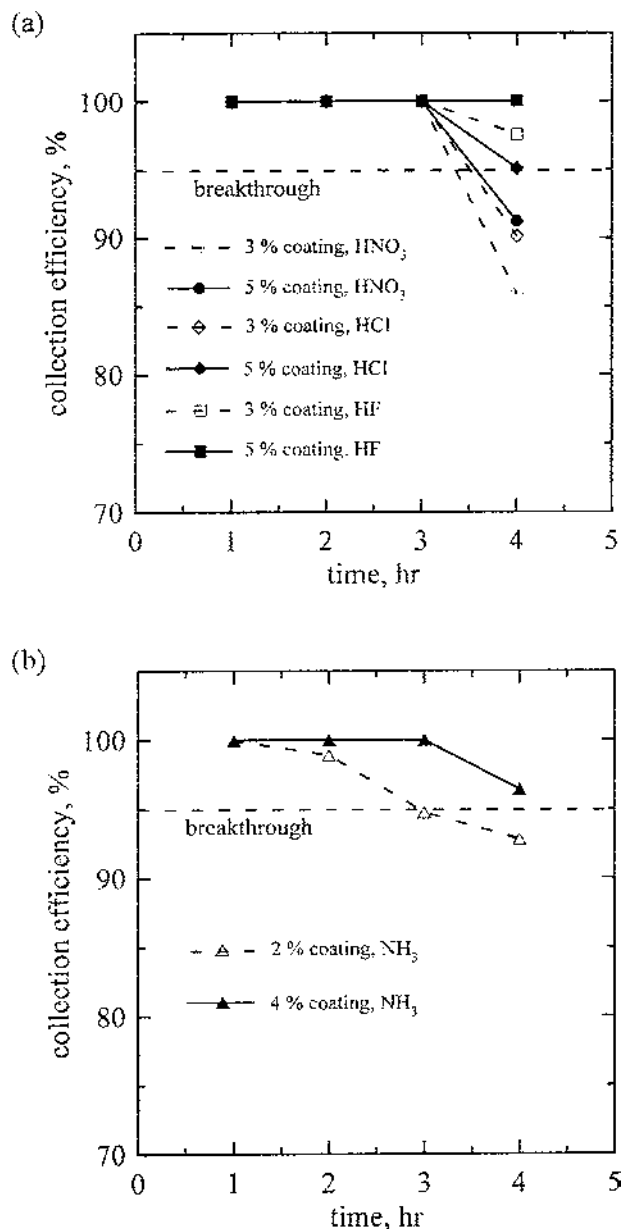


Figure 6. Gas collection efficiency versus sampling time. (a) acidic gas and (b) ammonia.

Results from Gas Experiments

Figures 6a and b show the gas collection efficiency of the porous-metal disc for acidic and basic gases, respectively. Using a 3% sodium carbonate coating, the gas collection efficiencies are all close to 100%, as shown in Figure 6a, for HNO₃, HCl, and HF when the sampling time is < 3.0 h. However, the efficiency drops to $85.89 \pm 0.36\%$ (average \pm standard deviation) and $90.1 \pm 0.45\%$ for HNO₃ and HCl, respectively, at the sampling time of 4.0 h. Increasing the sodium carbonate concentration to 5%, the efficiency at 4.0 h is increased to $91.2 \pm 0.26\%$ and $95.08 \pm 0.06\%$ for the above two gases, respectively. For HF, the gas collection efficiency remains high at $97.57 \pm 0.05\%$ and $100 \pm 0.4\%$ for the sodium carbonate coating concentration of 3 and 5%, respectively.

For 3% sodium carbonate coating concentration, the breakthrough time (time at which the collection efficiency drops to 95%) is 3.35, 3.5, and 4.0 h for HNO₃, HCl, and HF, respectively. The maximum breakthrough time is assumed to be 4.0 h as in the case of HF. The breakthrough time is increased to 3.58 and 4.0 h for HNO₃ and HCl, respectively, when the coating concentration is increased to 5%. The gas collection capacity of the porous-metal disc is calculated to be 4.18, 6.3, and 2.5 mg for HNO₃, HCl, and HF, respectively, at 3% coating concentration. It is increased to 4.47 and 7.2 mg for HNO₃ and HCl, respectively, when the coating concentration is increased to 5%. Since the maximum breakthrough time is 4.0 h, the capacity for HF remains the same at 2.5 mg for 5% coating concentration.

Similarly, Figure 6b shows that different citric acid coating concentrations also result in different NH₃ collection efficiencies and capacities by the porous-metal disc. Increasing the concentration of citric acid coating solution from 2 to 4% increases the efficiency at 4.0 h from $92.8 \pm 0.14\%$ to $96.39 \pm 0.13\%$ and the breakthrough time is increased from 2.9 to 4.0 h. The corresponding collection capacity for 2 and 4% coating concentration is 24.36 mg and 33.6 mg, respectively.

CONCLUSION

This study extended the work of Wai et al. (1994) and showed that it is possible to use the porous-metal disc as a personal denuder for sampling high concentrations of acidic and basic gases in the laboratory. The gas collection efficiency and capacity of the denuder with suitable coating material and concentration will be sufficiently high for the 8 h sampling in the workplace, providing that the gas concentration is below the PEL.

Because loss of particles in the porous-metal disc may lead to interference with the gas concentration measurement, incorporating a particle classifier to remove large particles before the porous-metal discs is necessary. This study uses a 2 stage cascade impactor for this purpose. To prevent a particle overloading problem, porous-metal discs were used as impaction substrates to collect high concentration liquid aerosol particles that may exist in the workplace. The experimental data showed that the cut-off diameters are smaller than that predicted by Marple's

theory, presumably due to excess particle collection because of partial air penetration into the porous-metal substrates. Further study of the particle collection characteristics and the loading effect of the impactor is necessary.

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