

Evaluation of Commercial Air-Purifying Respirator Cartridges for Protection against Vapors of Nitric Acid

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Introduction

Nitric acid is widely used at LANL; however, the effectiveness of air-purifying respirator acid gas cartridges in protecting workers from vapors of nitric acid is not well established. The National Institute for Occupational Safety and Health and Mine Safety and Health Administration certify cartridges for some acid gases, but not nitric acid. Consequently, ventilation, engineering controls, and air-line respirators (with air-purifying cartridges for escape only) are relied upon for routine operations involving nitric acid. However, for spills or leaks outside of hoods or normal work areas, the only currently documented protection is for use of a self-contained breathing apparatus.

The objective of this work has been to determine whether and under what conditions the cartridges available at the Laboratory are effective in removing vapors of nitric acid so that they can be confidently used with air-purifying respirators.

Progress and Results

We selected two air-purifying respirator cartridges in use at LANL for this study: Mine Safety Appliances (MSA) Company Combination Cartridge GMC-H and MSA Combination Cartridge GME-H. We packed samples of the carbons from these cartridges into a fluorocarbon tube of inner diameter 2.1 cm and passed total air flows of 2-3 L/min through the bed. Carbon sample weights were scaled to correspond at a total testing flow of 2 L/min to the same residence time as one full cartridge at 25 L/min and an average total

breathing rate of 50 L/min (two cartridges). Smaller (1/4, 1/2, 3/4) beds were also tested.

The nitric acid vapors were generated by passing a purge air flow (10-60 mL/min) through a chamber in which concentrated nitric acid was being stirred. The nitric acid output was calibrated before and/or after each test by using an empty tube in place of a test bed. Acid vapor concentration increased with increasing purge air-flow rate. Nitric acid in bed effluent air or challenge air (empty tube) was measured by continuously drawing part (about 1 L/min) of the effluent air through a bubbler containing 200 mL of water. A pH probe immersed in the bubbler allowed continuous pH measurements with a meter that sent the values to a computer for data acquisition at 1-min intervals. For some tests, we humidified test air by passing it through a chamber containing water. Relative humidity (RH) and temperature (T) were monitored using a dew-point hygrometer upstream of the mixing point.

We put the pH measurements taken at 1-min intervals into a spreadsheet and converted them to acid concentrations. The average slope of concentration vs. time over a selected time interval was obtained by linear regression. It was then converted to an average acid vapor concentration using the bubbler water volume and local atmospheric conditions. The time interval selected for the results reported here was the first 60 minutes. We consider this the most important time interval for the usual application of starting with a freshly opened cartridge. Measurements were actually continued for hours or even days. However, apparent acid breakthroughs (or ammonia

desorptions) dropped off after the first hour and only increased much later. Average apparent breakthrough fraction over the first 60 min was calculated by taking the ratio of average nitric acid concentration in the effluent and the challenge concentration measured before or after the test.

Figure 1 shows a logarithmic plot of measured average breakthrough fractions vs. amounts of GMC-H carbon (the highest weight corresponds to a full-size bed). The most important observation from these tests is that all full-bed equivalent (3.765 g average) measurements at dry and humid conditions showed nitric acid breakthrough fractions less than 0.01 (1%). For the dry (< 25% RH) condition tests with both full and partial bed size equivalents, there were no apparent effects of nitric acid challenge concentration (31-342 ppm), relative humidity (7-25%), or airflow rates (1.95-2.79 L/min). Tests in the 54-60% RH range for 1/4-bed equivalents gave breakthrough fractions in the same range as those obtained at lower relative humidities.

At relative humidities higher than 60% RH, negative apparent breakthrough concentrations and fractions were obtained. These reflect the observation that the sampler water actually decreased in acidity. This will be discussed below. Tests with GME-H carbon full-bed equivalent (5.5 g) tests at dry (< 25% RH) conditions all showed apparent nitric acid breakthrough fractions of 0.0025 (0.25%) or less. The apparent nitric acid breakthrough vapor concentrations increased with challenge vapor concentration. The most interesting observation

in the GME-H tests is that for some blank (no acid challenge) tests and some acid challenge tests at all humidities (19–90% RH), the acidity of the sampler waters decreased. The apparent nitric acid breakthrough concentrations were more negative at higher relative humidities with the GME-H carbon.

The decreases in sampler water acidity mentioned above were attributed to ammonia or some organic amine desorbing from the respirator cartridge carbons. Common practice is to use ammonia salts to enhance the carbon reactivity. After discussions with MSA and Calgon, we concluded that it must be ammonia desorbing from the carbons. This conclusion was confirmed by a mass spectrometric study of the effluent from GME-H carbon. Clear signals at mass peaks 15, 16, and 17 that correspond to the fractionation pattern of ammonia were observed. We saw no other significant mass peaks corresponding to other compounds. Therefore, the negative apparent acid breakthroughs can be taken to be concentrations of ammonia desorbing from the carbons at the test conditions. Figure 2 shows that the ammonia desorption from GME-H becomes most pronounced at relative humidities above 70%. The highest ammonia concentration measured in the first 60 min was 5.5 ppm at 86% RH. Although the GMC-H data are less extensive, it suggests a similar conclusion, with a maximum of 1.7 ppm observed at 73% RH.

These maximums are both well below the ammonia TLV of 25 ppm, but even low releases may be of concern to users sensitive to ammonia. There may also be a right-to-know issue for users. Fortunately for users of these cartridges at Los Alamos, the ambient relative humidity is usually low. Because GMC-H carbon (at least the batch studied) releases less ammonia, GMC-H cartridges might be preferred over GME-H cartridges.

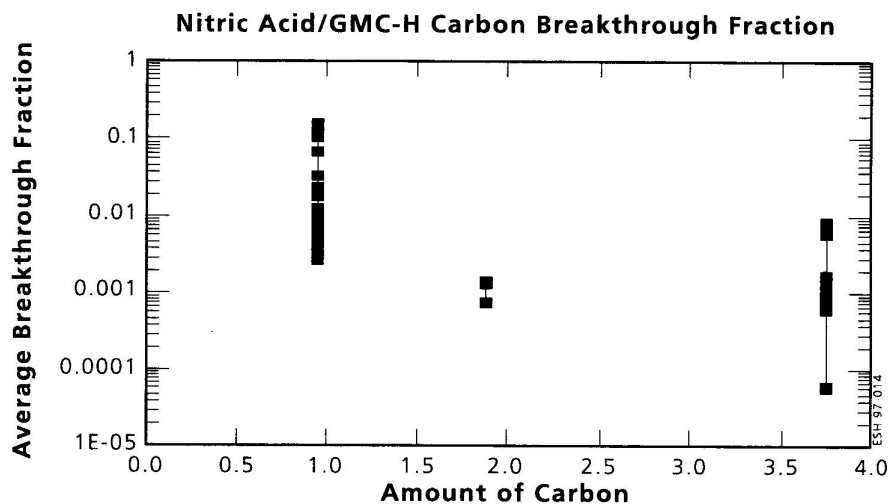


Figure 1. The effect of amount of carbon in a test bed on observed nitric acid breakthrough fractions

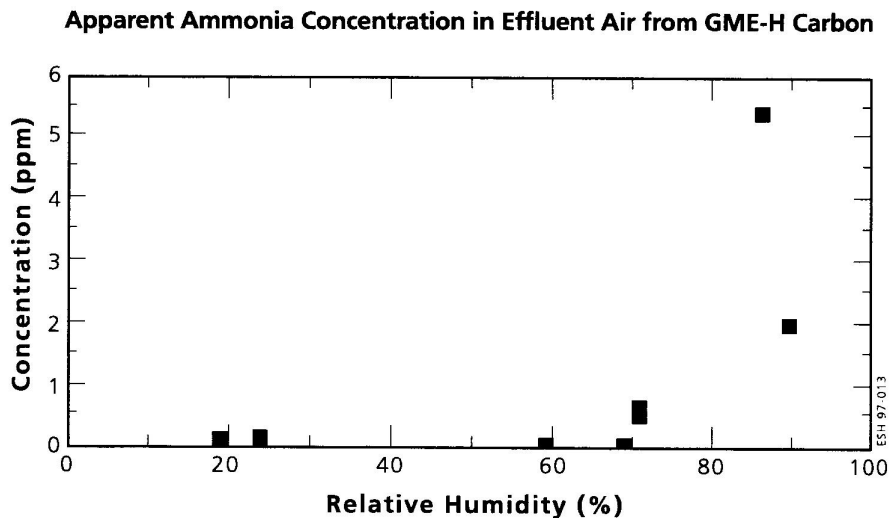


Figure 2. The effect of relative humidity on the release of ammonia from the GME-H carbon

The major conclusion of this study is that both cartridges are very effective in removing nitric acid vapors (>99% removal) from air for at least an hour even at

- low and high humidities,
- high nitric acid vapor concentrations, and
- air flow rates corresponding to breathing at moderately heavy work (50 L/min).

Deliverables

The following are project deliverables:

- Final progress report, October 1996.
- Abstract submitted for presentation at the 1997 American Industrial Hygiene Conference and Exposition, October 1997 (acceptance pending).
- Article for publication in the American Industrial Hygiene Association Journal.

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