CHEMICAL CARTRIDGE CHANGE OUT SCHEDULES

BACKGROUND:

Ref: (a) 29 CFR 1910.134
(b) Nelson, T.J., Colton, C., Nelson, G., and Wood, G.: Respirator Cartridge Replacement Schedules Workshop. American Industrial Hygiene Conference and Exposition. June 6, 1999. Toronto, Canada.
(c) Nelson, T. J. and Janssen, L.L.: Developing Cartridge Change Schedules: What are the Options? 3M JobHealth Highlights 17(1):1-8 (1999).
(d) Wood, Gerry O.: Estimating Service Lives of Organic Vapor Cartridges. Am. Ind. Hyg. Assoc. J. 55(1): 11-15 (1994).
(e) NAVMCPUBHLTHCEN Technical Manual, Industrial Hygiene Field Operations Manual, latest revision
(f) Joselito, I.S. and Bullock, W.H., ed.: A Strategy for Assessing and Managing Occupational Exposures. Fairfax, VA: AIHA Press, 2006.
(g) CONVERSATION NAVMCPUBHLTHCEN Mr. Wright/ NAVMCPUBHLTHCEN Mr. Spelce of 13 Apr 00
(h) Industrial Hygiene Sampling Guide For Consolidated Industrial Hygiene Laboratories, latest revision
(i) OSHA Instruction, CPL 2-0.120, Inspection Procedures for the Respiratory Protection Standard of 25 Sep 98, as revised 14 Jul 2004
(j) National Institute for Occupational Safety and Health. A Guide to Industrial Respiratory Protection. NIOSH Pub. 76-189. Cincinnati, OH: U.S. Department of Health, Education, and Welfare. 1976. 150 p.
(k) E-Mail NIHS, Inc. Mr. Nelson/NAVMCPUBHLTHCEN Mr. Spelce of 9 Jul 99
(l) PHONCON OSHA Mr. Motley/ NAVMCPUBHLTHCEN Mr. Spelce of 4 Apr 00

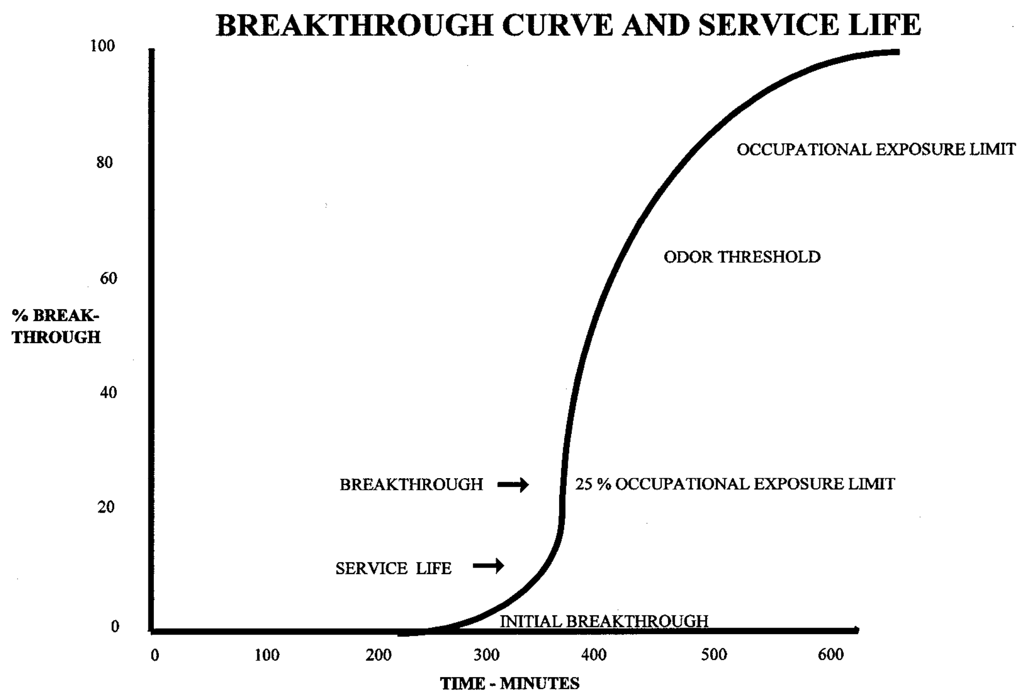
Appendix: (A) Estimating Breakthrough Time for Mixture Components

The Occupational Safety and Health Administration (OSHA), in paragraph (d)(3)(iii) of reference (a), states that reliance on odor thresholds and other warning properties is no longer permitted as the sole basis for determining that air-purifying respirators will afford adequate protection against exposure to gas and vapor contaminants. Employers are required to implement a change out schedule for chemical canisters and cartridges based on objective information or data that will ensure they are changed before the end of their service life. This data, along with the logic for relying on this change out schedule, must be described in the respirator program. Establishing cartridge change out schedules will require concerted efforts between respiratory protection program managers (RPPMs) and Bureau of Medicine and Surgery industrial hygienists. Cartridge change out schedules are required for both negative pressure and powered air purifying respirators.

The basis for change out schedules should ideally be based on tests of cartridge/canister breakthrough that are conducted under worst-case conditions of contaminant concentration, humidity, temperature and air flow through the filter element. If change out schedules are not developed and implemented, then either atmosphere-supplying respirators or, where they are available and appropriate for the workplace, air-purifying respirators equipped with end-of-service-life indicators (ESLIs) can be worn as protection against gases and vapors. Unfortunately, there are at this time ESLIs only for hydrogen sulfide, carbon monoxide, ethylene oxide, mercury, and vinyl chloride.

Breakthrough time is the length of time it takes for a gas or vapor to saturate sorbent material in chemical cartridges and then enter the respirator. Breakthrough time must further be defined as a specific concentration that is detected downstream of the cartridge sorbent bed under a given set of environmental variables. As discussed below, there are many different factors affecting breakthrough time for different organic vapors and mixtures of organic vapors. Figure (1), which was adapted from reference (b), shows that breakthrough can be defined on the typical breakthrough curve as any time from initial breakthrough up to just below the occupational exposure limit. For this protocol, breakthrough is defined on the breakthrough curve as when breakthrough has reached 25% of the occupational exposure limit.

Figure 1



According to paragraph (b) of reference (a), "Service life means the period of time that a respirator, filter or sorbent, or other respiratory equipment provides adequate protection to the wearer." Cartridges should ideally be changed before expected breakthrough. Therefore, apply a safety factor, such as changing cartridges before 90% of the estimated breakthrough time (e.g., for an estimated breakthrough time of 100 minutes, change cartridges by at least 90 minutes of use). As shown in Figure 1, breakthrough (25% of the occupational exposure limit) occurs after 380 minutes. After applying the safety factor, the service life is 342 minutes (380 min X 90% = 342 min). For convenience, the change out schedule could be set to change cartridges after a four hour shift (240 minutes). Depending on the calculated service life, change out schedules will usually be designated at four hours, eight hours, one week, or some other time that is convenient for changing cartridges.

The service life of a cartridge is affected by many variables including: (1) workers' breathing rate (service life is inversely proportional to breathing rate); (2) adsorbing capacity of the chemical cartridges (more sorbent material provides greater service life); (3) temperature (every 10^{O} C increase can reduce service life up to 10%); (4) relative humidity (humidity above 85% can reduce organic vapor service life by 50%, since water vapor displaces organic vapors from the sorbent material; and (5) concentration of contaminants in the workplace (reducing concentration by a factor of 10 will, in general, increase service life by a factor of five). OSHA has developed "rules of thumb" based on these factors, which can be used to estimate service life of respirator cartridges. **Warning - these statements do not generally apply to inorganic gases (e.g., sulfur dioxide, hydrogen sulfide) although some manufacturers' are developing calculators that will estimate their breakthrough time**. Humidity increases the service life of inorganic gas sorbents because inorganic gases are soluble in water.

Most mathematical models for calculating breakthrough time are based on the exposure from a single contaminant and are strongly influenced by high humidities. Exposures in most workplaces are from mixtures of contaminants and high humidity is a common problem. The procedure described below will allow determination of change out schedules for atmospheres containing operationally important mixtures of contaminants in high humidities.

PROCEDURE OVERVIEW:

The following procedure is based on the information provided in references (b) and (c) and will allow determination of service life of the chemical cartridges used for protection against mixtures of organic vapors. The objective is to determine that breakthrough has not occurred prior to changing cartridges, rather than to determine the exact time breakthrough occurs.

The method first requires characterization of the chemical exposure concentrations in the workplace. The second step involves estimating breakthrough times for each organic component of the mixture by using one of the respirator manufacturers' chemical cartridge service life calculators or OSHA's "Advisor Genius" calculator. Most chemical cartridge service life calculators will ask you to select a safety factor for high humidities. Most of these calculators are based on Wood's equation shown below, and described in detail in reference (d).

WOOD'S EQUATION

$$t_b = \left(\frac{W_e W}{C_o Q}\right) - \left(\frac{W_e \rho_\beta}{k_v C_o}\right) \ln\left[\frac{C_o - C_x}{C_x}\right]$$

where

t_b = breakthrough time (min)
C_x = exit concentration (g/cm^3)
C_o = inlet concentration (g/cm^3)
Q = volumetric flow rate (cm^3/min)
W = weight of carbon adsorbent (g)
ρ_β = bulk density of the packed bed (g/cm^3)
W_e = equilibrium adsorption capacity (g/g carbon)
k_v = adsorption rate coefficient (min^{-1}).

Next, calculate the estimated breakthrough time for each organic component relative to the proportion of their presence in the mixture. This is based on the mole fraction of the components in the mixture. Select a change out time for the mixture that is at least 10% less than that of the component with shortest breakthrough time.

In the workplace, verify the cartridge change out schedule by determining the presence or absence of organic vapor at change out time by sampling behind the cartridge while it is being worn. Sampling behind the cartridge is accomplished by using a PortaCount® quantitative fit test mask sampling adapter (Figure (2)) and a sampling method capable of detecting concentrations below the occupational exposure limits of the contaminant(s) of concern. Sampling behind the cartridges during the operation incorporates those factors, which are problematic to mathematical modeling (i.e., humidity, temperature, atmospheric pressure, breathing rate, and varying concentrations of multiple contaminants), into an empirical measurement that determines the presence or absence of chemical breakthrough.

Figure (2)
Fit Test Adapter

PROCEDURE DETAILS:

Step 1 - Characterize the workplace.

Determine the frequency and duration of exposure for employees wearing respirators for protection against gas and vapor contaminants. Ideally, the Upper Tolerance Limits ($UTL_{95\%, 95\%}$), the concentrations below which we are 95 percent confident that 95 percent of exposures lie, should be determined by following the strategies in Chapters 3 and 4 of reference (e). For a detailed explanation of the exposure assessment process consult reference (f). Chapter four of reference (e) states that six to ten samples from randomly selected members of a "similar exposure group" are required to allow statistically valid inferences to be drawn. In the absence of $UTL_{95\%, 95\%}$ concentrations, use the worst case exposure data to estimate exposure.

The following exposure data will be used to illustrate establishing respirator cartridge change out schedules with this method:

> Air monitoring determined the following workplace $UTL_{95\%, 95\%}$ concentrations: 65 ppm toluene, 60 ppm n-hexane, 75 ppm isobutyl acetate, 15 ppm ethyl benzene, 10 ppm trimethyl benzene, and 60 ppm xylene. Employees use the respirator for 7 hours during an 8 hour shift.

Step 2 - Estimate the breakthrough time for each component of the mixture.

Use the respirator manufacturers' chemical cartridge service life calculators or the OSHA Advisor Genius calculator to determine the breakthrough time for each component of the mixture. See Appendix (A) for details.

Mixture Component	**Cartridge Service Life Calculator Estimated Breakthrough Time For Single Component (Hours)**
toluene	83.37
n-hexane	48.93
trimethyl benzene	595.08
isobutyl acetate	64.62
ethyl benzene	340.87
xylene	103.5

Step 3 - Calculate the breakthrough time for the mixture and the cartridge change out schedule.

Calculate the mole fraction of each mixture component in the workplace based on its $UTL_{95\%, 95\%}$ concentration or worst case exposure data. Mole fraction is calculated by dividing concentrations of each mixture component in parts per million (ppm) by total ppm of the mixture.

Based on the mole fraction of the components in the mixture, calculate the estimated breakthrough time for each mixture component relative to its proportion of the mixture (mole fraction times computer calculated breakthrough time). As shown in Table 1, the breakthrough time of the mixture components relative to their mole fractions of the mixture is considerably reduced from the breakthrough times calculated on the chemical cartridge service life calculator.

TABLE 1 CALCULATE BREAKTHROUGH TIME OF COMPONENTS BASED ON THEIR PROPORTION OF THE MIXTURE				
Mixture Component	$UTL_{95\%, 95\%}$ Concentration (ppm)	Mole Fraction	Cartridge Service Life Calculator Estimated Breakthrough Time for Single Component (Hours)	Breakthrough Time of Components Based on Mixture (Hours)
Toluene	65	0.2282	83.37	19.03
n-hexane	60	0.2108	48.93	10.31
Trimethyl Benzene	10	0.0351	595.08	20.89
Isobutyl Acetate	75	0.2630	64.62	16.99
Ethyl benzene	15	0.0526	340.87	17.92
Xylene	60	0.2103	103.5	21.77
Total ppm	285			

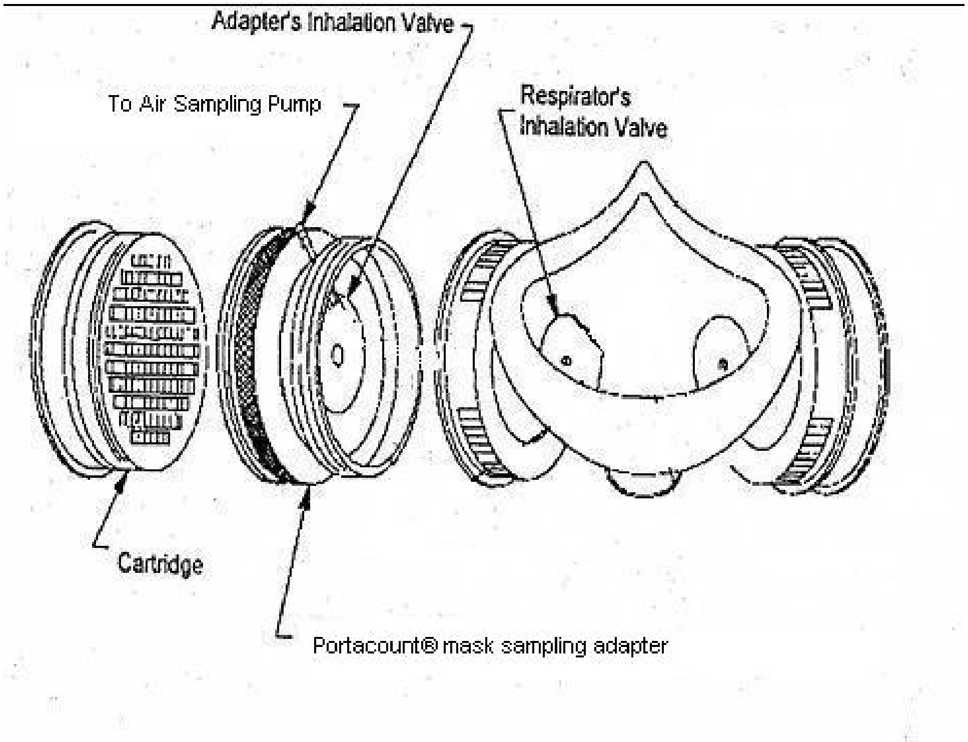
Base change out schedule on the shortest mixture component breakthrough time. Incorporate a safety factor, by selecting a change out schedule that is at least 10% less than the shortest mixture component breakthrough time. In this case, n-hexane has the shortest breakthrough time (10.31 hours) relative to the mixture. Ten percent of 10 hours is 1 hour. Therefore, the change out schedule must be 9 hours or less. Since the respirators are worn for a full shift, it would be convenient to change cartridges after one eight hour shift. This would also cause any "error" to be on the conservative side. Count the morning and afternoon breaks along with lunch time as an hour of continuous respirator use during the shift, due to possible chemical migration inside the cartridge.

Step 4 - Field testing.

In the workplace, collect an air sample behind the cartridge using a PortaCount® mask sampling adapter (see Figure 3). Collect these samples in the same workplace where the respirator use is required and while the process is ongoing. The sampling method (e.g., flame ionization detector, photoionization detector, hydrocarbon detector tubes, gas chromatograph, charcoal tube, etc) does not have to be specific for each component of the mixture but it should be sensitive enough to detect concentrations at 25 % of the occupational exposure limits of the mixture components. If no organic vapors are detected then the change out schedule is verified.

A list of mask sampling adapters available from respirator manufacturers is provided by TSI. Install the PortaCount® mask sampling adapter on the respirator in an area free of contaminated air, and then return to the worksite to collect the sample behind the cartridge while the respirator is being worn by the worker.

Figure 3
PortaCount® mask sampling adapter



To sample behind cartridges with the PortaCount® mask sampling adapter, take the employee to a non-contaminated area:

Ensure that the "Sample Tube," the "Suction Cup" and "Clip" (shown in Figure 2), which are connected inside the respirator only during fit testing, are removed from the mask sampling adapter.

Install the mask sampling adapter between the facepiece and the cartridge as shown in Figure 3.

Attach air sampling tubing to the outside fitting of the mask sampling adapter (Figure 3).

Have worker redon the respirator.

Attach the air sampling pump to the end of this tubing. Hang pump on workers' belt.

When back in the worksite, turn on the air sampling pump.

In this arrangement, the air sample will be collected in the chamber between the inhalation valve of the mask sampling adapter and the inhalation valve of the facepiece.

If there are no organic vapors detected in the samples then significant breakthrough (< 25% occupational exposure limit) has not occurred and the change schedule is confirmed. Change cartridges according to the estimated (**now verified**) change schedule.

It is not necessary for the Navy to purchase any additional air sampling equipment to collect air samples behind respirator cartridges for verifying cartridge change out schedules. Per reference (g), it is acceptable to collect air samples on sorbent tubes behind the cartridges at the highest flow rate allowed by reference (h). This permits relatively quick collection of the lowest sample volume, allowed by reference (h), for laboratory analysis results that can be reported in concentrations down to the limit of detection. Most air samples can be collected behind cartridges in five to ten minutes.

NAVMCPUBHLTHCEN performed an experiment to determine if workers' breathing would interfere with the flow rate of sampling pumps while collecting air samples behind the cartridges. Most gas/vapor contaminants will be sampled for at 0.2 liters per minute (lpm). An analysis of variance (ANOVA) test of the experimental results showed that there is no significant difference ($P_{0.05}$) between the average flow rate of pumps collecting air samples in ambient atmosphere and pumps collecting air samples inside PortaCount® mask sampling adapters connected to workers' respirators while they breath normally. However, ANOVA indicated that there is a significant difference ($P_{0.05}$) between those two means and the mean flow rate of pumps collecting air samples inside PortaCount® mask sampling adapters connected to workers' respirators while they are breathing hard. Therefore, when an air sample is collected behind a cartridge inside a PortaCount® mask sampling adapter, the worker must breathe normally so as not to interfere with collection of the sample. Instruct the worker to take a break for 5 to 10 minutes while wearing the respirator in the worksite during air sample collection. The workers' normal breathing will not adversely influence detection of breakthrough. By the time of air sample collection, all of the varying air contaminant concentrations, varying temperature and humidity, and varying breathing rates throughout the day have already had their influence on respirator cartridge breakthrough. In other words, workers breathing normally right before cartridge change out time would not significantly influence breakthrough – breakthrough would have either already occurred or not occurred.

Step 5 - Record Entry.

Once confirmed in the workplace, the change out schedule along with the supporting data must be incorporated in the written respirator program. Include the following information: (1) frequency and duration of the operation and the $UTL_{95\%, 95\%}$ or worst case exposure concentrations for the contaminants in the operation; (2) temperature, relative humidity, and worker breathing rate; (3) estimated breakthrough time for individual mixture components from cartridge service life calculator; (4) calculations showing mole fraction and breakthrough time of the mixture components relative to their mole fraction in the mixture; (5) estimated change out schedule for the mixture; and (6) results of air sampling behind the cartridges.

OTHER AREAS OF CONCERN:

The focus of this paper has been on determining cartridge change out schedules for mixtures of organic vapors. There will be instances where a change out schedule must be determined for a single component. In this case, characterize the workplace exposure as described in step 1. Use the respirator manufacturers' chemical cartridge service life calculators or the OSHA Advisor Genius calculator to determine the breakthrough time for the single component. Set a convenient change out schedule at least 10% less than the estimated breakthrough time. Collect an air sample behind the cartridge using a PortaCount® mask sampling adapter to verify the change out schedule.

According to paragraph E.(3) of reference (i), "Where an effective change schedule is implemented, air-purifying gas and vapor respirators may be used for hazardous chemicals, including those with few or no warning properties." This means that air-purifying respirators can be used for protection against isocyanates where cartridge change out schedules are established and implemented.

In some instances, low toxicity mixture components with low mole fractions and low concentrations have short estimated breakthrough times. Consider a workplace exposure where the ethane trichloride (1,1,2-Trichloroethane) concentration is above the 10 ppm permissible exposure limit (PEL) and the concentrations for isopropanol and ethyl acetate are less than 25% of their 400 ppm PELs. Isopropanol and ethyl acetate have short breakthrough times but 1,1,2-trichloroethane has a much longer breakthrough time. Should we use the longer estimated breakthrough time for 1,1,2-trichloroethane instead of the estimated breakthrough time for isopropanol and ethyl acetate? We could sample behind the cartridge specifically for 1,1,2-trichloroethane. In this case, we are not as concerned about the health effects caused by breakthrough of isopropanol and ethyl acetate in concentrations less than 25% of the PELs since we are more appropriately protecting the worker against 1,1,2-trichloroethane exposure.

If sampling behind the cartridges does detect breakthrough (> 25% of occupational exposure limits) then reevaluate workplace air sampling results, chemical cartridge service life calculator estimates, and mole fraction calculations. If breakthrough concentration is >25%, worker exposure would not be greater than that measured behind the cartridges.

For mixtures in which the components are not listed, sample for the most characteristic component of the mixture. For example: in a mixture of hydrocarbons, which does not identify the components, sample for octane.

Special care should be taken for chemicals with boiling points below 65°C (149°F) if used after one shift because they are not adsorbed well by the activated charcoal and may migrate through the cartridge. This is especially a problem if the end of the shift is on Friday and the cartridges are stored over a weekend instead of just overnight. Use the PortaCount® mask sampling adapter to sample behind the cartridges prior to use and periodically throughout the day to ensure low boiling point chemicals have not migrated through the sorbent material and into the facepiece.

Do not use chemical cartridges for chemicals that have breakthrough times less than 15 minutes.

Reference (a) states that cartridge change schedules should ideally be based on tests of breakthrough studies that are conducted under worst-case conditions of contaminant concentration, humidity, and temperature and air flow through the filter element. The worst-case climatic conditions for reducing cartridge service life would occur during the summer months. For economical reasons, consideration should also be given to establishing a change out schedule for the winter months when climatic conditions should allow longer use of cartridges.

Use of chemical cartridge, air-purifying respirators range from operations where overexposure to vapors and gases have been documented to the other end of the spectrum where employees voluntarily request to wear respirators when they are not exposed to hazardous vapors and gases. Highest priority for establishing and verifying respirator cartridge change out schedules should start with operations with documented overexposures. This category of operations comprises only a small portion of total respirator use in the Navy.

Next priority would be to establish cartridge change out schedules for respirators that are recommended in industrial hygiene survey reports or provided by Respiratory Protection Program Managers (RPPMs) for worker protection when overexposure does not occur. This category comprises the majority of air-purifying respirator use. For example, evaluation of degreasing, wipe cleaning operations (IND-002-06) data from the Navy Occupational Exposure Database revealed that 95% of the respirators worn during these operations were worn when contaminant concentrations were below the action level. Only 3% of respirator use was actually worn as protection against contaminant concentrations exceeding the occupational exposure limits (OELs). For worker protection, it is necessary to establish cartridge change out schedules for this category of respirator wear even though contaminant concentrations are below the OELs. Vapors/gases have an affinity for activated and treated charcoal and will adsorb on the charcoal bed even at low ambient workplace concentrations. Breakthrough will eventually occur due to chemical desorption of the vapors/gases and their migration through the cartridge charcoal bed. When this occurs, the concentration of contaminants inhaled by the respirator wearer would be higher than contaminant concentrations found in the ambient workplace atmosphere. One answer to this problem would be to not recommend nor issue respirators where worker exposure does not warrant their use. If the operations in this category were carefully characterized with respect to proper worker protection, most of the Navy's respirator use could be eliminated.

The lowest priority would be voluntary respirator use, when employees request respirators when there is no risk of personal overexposure. According to reference (l), change out schedules would not have to be established for voluntary respirator use. The validity of the prioritization plan shown in Table 2 for establishing respirator cartridge change out schedules was verified per reference (l).

Table 2
Priority For Establishing
Respirator Cartridge Change Out Schedules

First Priority		Second Priority		Last Priority
Documented Overexposure	→	Unnecessary Respirator Use	→	Voluntary Respirator Use

POC:
David L. Spelce, MS, CIH
Navy and Marine Corps Public Health Center
Industrial Hygiene, Acquisition Technical Support Division
620 John Paul Jones Circle
Portsmouth, VA 23708-2103
DSN: 377-0719 or (757) 953-0719
FAX: (757) 953-0689
E-mail address: David.Spelce@med.navy.mil

APPENDIX A
ESTIMATING BREAKTHROUGH TIME FOR MIXTURE COMPONENTS

Use the respirator manufacturers' chemical cartridge service life calculators, the OSHA Advisor Genius calculator, or the *NIOSH MultiVapor Beta Version 2.1.3* to determine the breakthrough time for each component of the mixture. Most chemical cartridge respirator manufacturers offer free respirator cartridge service life software, based on Wood's mathematical model, to estimate respirator cartridge change out schedules. The software requires characterization of workplace chemical concentrations and workplace environmental data. Each manufacturer's software is specific for their cartridges.

OSHA's Advisor Genius service life software can calculate breakthrough times for any manufacturers' cartridges if pertinent information is know about the manufacturers' sorbent material such as the: (1) weight of sorbent in the cartridge in grams; (2) bulk density of the packed sorbent bed in g/cm^3; (3) carbon micropore volume in cm^3/g; and (4) diameter of the cartridge bed in centimeters.

NIOSH MultiVapor Beta Version 2.1.3 calculator can be used to estimate respirator cartridge breakthrough of a mixture of organic vapors or a single component at any humidity. It requires: 1) parameters of the cartridge and the carbon it contains; 2) physical characteristics of the vapor(s) present; and 3) environmental and use conditions.

The calculators require information on temperature, relative humidity, and worker breathing rate. The breathing or work rate is in liters of air per minute (l/min). Estimate the average breathing rate for the worker during the work period that the respirator is worn. Reference (j), states that "The typical worker breathes about 10 cubic meters (m^3) of air in 8 hours." This converts to 20.8 l/min. Caution! Many respirator manufacturers' chemical cartridge service life calculators default to higher breathing rates (the OSHA Advisor Genius calculator defaults to 60 l/min.). Per reference (k), good estimates for low, moderate, and high work rates are 20, 40, and 60 l/min, respectively. Per reference (b), use 30 l/min for most applications because higher work rates cannot be sustained for long periods of time.

Most calculators require that you select the breakthrough concentration as a percentage of the occupational exposure limit. Select 25% of the occupational exposure limit. However, the OSHA Advisor Genius calculates breakthrough based on 10% of the workplace concentration.

The OSHA, NIOSH, and manufacturers' chemical cartridge service life calculators are available from the following sources:

OSHA Advisor Genius calculator:
http://www.osha.gov/SLTC/etools/respiratory/mathmodel_advisorgenius.html

NIOSH MultiVapor Beta Version 2.1.3
http://www.cdc.gov/niosh/npptl/multivapor/multivapor.html

3M Respirator Service Life Software
http://solutions.3m.com/wps/portal/3M/en_US/Health/Safety/Resources/Four/

MSA Cartridge Life Expectancy Calculator:
http://webapps.msanet.com/cartlife/

AOSafety Merlin Cartridge Change Out Program Software & Respirator Selection Guide
http://www.aosafetyproducts.com.mx/Admin/files/20070305153243.pdf

Survivair Cartridge Service Life Software
http://www.survivair.com/support/cartridge.asp and
http://www.survivair.com/support/downloads.asp

North Safety Products - Selection Guide for Respiratory and Hand Protection calculates estimated cartridge service life.
http://www.northsafety.com/

SCOTT provides cartridge change-out data information on over 120 compounds for use with Scott’s 642 Organic Vapor, Organic Vapor/Acid Gas, and Multi-Purpose cartridges. This information is available on CD-ROM, 3.5” floppy disk or hard copy and can be used with Microsoft® Excel version 5.0 or later. Data on inorganic compounds is also available upon request. For a free copy call (800) 247-7257.