

SANDIA REPORT

SAND2013-4794
Unlimited Release
Printed June 2013

Safe Handling of Potential Peroxide Forming Compounds and Their Corresponding Peroxide Yielded Derivatives

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Abstract

This report addresses recent developments concerning the identification and handling of potential peroxide forming (PPF) and peroxide yielded derivative (PYD) chemicals. PPF chemicals are described in terms of labeling, shelf lives, and safe handling requirements as required at SNL. The general peroxide chemistry concerning formation, prevention, and identification is cursorily presented to give some perspective to the generation of peroxides. The procedure for determining peroxide concentrations and the proper disposal methods established by the Hazardous Waste Handling Facility are also provided. Techniques such as neutralization and dilution are provided for the safe handling of any PYD chemicals to allow for safe handling. The appendices are a collection of all available SNL documentation pertaining to PPF/PYD chemicals to serve as a single reference.

ACKNOWLEDGMENTS

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NOMENCLATURE

DOE	Department of Energy
SNL	Sandia National Laboratories
PPF	Potential Peroxide Forming
PYD	Peroxide Yielded Derivative

1. INTRODUCTION

This report was written to address recent concerns at Sandia National Laboratories (Sandia) concerning the safe handling of potential peroxide forming (PPF) compounds and those that have formed an unacceptable level of peroxide ['peroxide yielded derivative' (PYD)]. Changes to the Chemical Inventory System (CIS) that are expected to occur this year will mitigate this issue; however, until that time, the major goal of this report is to summarize the information related to PPF/PYD compounds to ensure safe handling, including (i) a cursory discussion of labeling and recommended shelf lives, (ii) peroxide chemistry in terms of formation, prevention, and identification (as of May 2013), (iii) safe handling and disposal requirements (iv) the Hazardous Waste Handling Facility's procedure for determining peroxide concentrations, (v) peroxide neutralization chemistry, (vi) a procedure for yielding acceptable peroxide concentration levels, and (vii) a description of successful neutralization and dilution techniques that allow for safe handling. The appendices of this document also serve as a single reference for all currently available Sandia peroxide documentation, including the May 2011 SAND report (2011-3509 P) on peroxidizable compounds, Industrial Hygiene (IH) documentation (e.g., ESH 100.2.IH.4 requirements and Guidelines for Peroxidizable Organic Chemicals), an example center (1800) OP in place at Sandia concerning PPF compounds (OP1804004 Issue D), commercial peroxide testing strip documentation, a peroxide test strip comparison exercise, and Hazardous Waste Handling Facility documentation (RF 2042-PFC and FOP 08-11). It is important that your manager, ES&H and IH personnel be involved with all concerns or issues regarding PPF/PYD chemicals.

1.1. Potential Peroxide Forming (PPF) Chemicals

Known PPF compounds have been conveniently grouped into three major classes based on the work of Jackson *et al.* and Kelly.^{1,2} These classes were developed based on the method of peroxide formation. Table 1 lists some examples of the different classes of PPF compounds (*note*: this is *NOT* an exhaustive list). The different classes are discussed below with SNL requirements from ESH 100.2.IH.4 on storage, handling, and disposal included for each.

Class A. These types of compounds can generate peroxides without concentration and may explode unexpectedly due to shock and heat sensitive (SNL: discard solids at manufacturer's expiration date, liquids within 24 months of initial receipt, and gases within 36 months of initial receipt).

Class B. These materials develop peroxides based on concentration (i.e., head space) due to evaporation or distillation (SNL: discard solids at manufacturer's expiration date, liquids within 24 months of initial receipt, and gases within 36 months of initial receipt).

Class C. These are typically unsaturated materials of low molecular weight that can polymerize (often violently) due to peroxide initiation. These materials must be stabilized or

decontaminated (SNL: discard solids at manufacturer's expiration date, liquids within 24 months of initial receipt, and gases within 36 months of initial receipt).

All potential peroxide materials must have a label (see below) with established routine schedule for testing as per Industrial Hygiene documentation (e.g., ESH 100.2.IH.4 requirements and Guidelines for Peroxidizable Organic Chemicals).


			CAUTION		
PEROXIDE FORMING CHEMICAL					
Date Received	__ / __ / __		INHIBITOR ADDED		
Date Opened	__ / __ / __		<input type="checkbox"/> Yes <input type="checkbox"/> No		
Date Expires	__ / __ / __		Type _____		
Limited shelf life. Store tightly closed away from light and heat.					
Test Date	_____	Peroxide	_____	Tester	_____
Test Date	_____	Peroxide	_____	Tester	_____

Figure 1 Example of a standard label required for PPF compounds

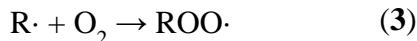
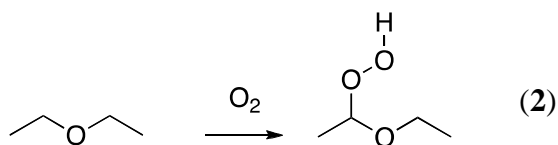
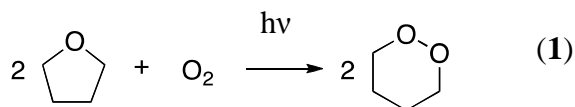
Table 1 Examples of Classes of potential peroxide forming (PPF) chemicals.³

Class A	
<i>Organic</i>	<i>inorganic</i>
butadiene (106-99-0)	
chloroprene (126-99-8)	sodium amide (7782-92-5)
Divinyl ether	potassium amide (17242-52-3)
divinylacetylene (31014-03-6)	potassium metal (7440-09-7)
isopropyl ether (108-20-3)	
tetrafluoroethylene (116-14-3)	
vinylidene chloride (75-35-4)	
Class B	
acetal (105-57-7)	methylacetylene (74-99-7)
acetaldehyde (75-07-0)	3-methyl-1-butanol* (123-51-3)
benzyl alcohol (100-51-6)	methylcyclopentane (96-37-7)
2-butanol* (78-92-2)	methyl isobutyl ketone (108-10-1)
cumene (98-82-8)	divinylacetylene (31014-03-6)
cyclohexanol* (108-93-0)	vinylidene chloride (75-35-4)
2-cyclohexen-1-ol (822-67-3)	tetrafluoroethylene (116-14-3)
cyclohexene (110-83-8)	4-penten-1-ol (821-09-0)
decahydronaphthalene (91-17-8)	1-phenylethanol (98-85-1)
diacetylene (460-12-8)	2-phenylethanol (60-12-8)
4-methyl-2-pentanol* (108-11-2)	2-propanol* (67-63-0)
diethyl ether (60-29-7)	tetrahydrofuran (109-99-9)
diethylene glycol dimethyl ether (111-96-6)	tetrahydronaphthalene (119-64-2)
dioxanes (123-91-1 or 505-22-6)	vinyl ethers
ethylene glycol dimethyl ether (110-71-4)	other secondary alcohols*
4-heptanol* (589-55-9)	dicyclopentadiene (77-73-6)
2-hexanol* (626-93-7)	cyclopentene
Methyl methacrylate	chlorotrifluoroethylene
Cyclooctene	furan
Class C	
acrylic acid (79-10-7)	styrene (100-42-5)
acrylonitrile (107-13-1)	tetrafluoroethylene (116-14-3)
butadiene (106-99-0)	vinyl acetate (108-05-4)
chloroprene (126-99-8)	vinylacetylene (689-97-4)
chlorotrifluoroethylene (79-38-9)	vinyl chloride (75-01-4)
ethyl methacrylate (97-63-2)	vinylpyridine (100-69-6)
methyl methacrylate (80-62-6)	vinylidene chloride (75-35-4)

*peroxide formation is typically slower unless concentrated

(b) Peroxide Formation Mechanism

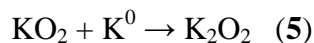
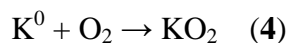
With any PPF chemical, peroxide formation should be anticipated; however, the mechanism of PPF compounds to PYD species for organic and inorganic compounds follows different routes and is discussed below to allow some understanding of how the peroxide forms to assist in mitigating this process.



For organic PPF compounds three oxygen insertion pathways have been presented: radical initiation (equation 1), molecular oxygen (O_2) insertion (equation 2), or peroxyradical generation (equation 3). For routes 1 and 2, an ether bond ($\text{R-O-R}'$) is a necessary requirement and the mechanism is catalyzed by light. Route 3 involves an organic radical that activates molecular oxygen. The insertion of molecular oxygen proceeds through weak carbon-hydrogen bonds or an activated hydrogen atom. Easily activated hydrogen atoms were recently reviewed^{4,5} and classified as containing:

- methylene groups ($-\text{CH}_2-$) adjacent to an ether oxygen,
- methylene groups attached to a vinyl group ($\text{C}=\text{C}-\text{CH}_2-$) or a benzene ring,
- methine groups ($-\text{CH}-$) between a benzene ring and a methylene group ($\text{Ph}-\text{CH}-\text{CH}_2$),
- vinyl groups ($-\text{C}=\text{CH}_2$).

In contrast, inorganic peroxide formation occurs by several different mechanisms mainly involving the $\delta+$ metal center (equations 4-5). For instance, upon exposure to O_2 , potassium metal (K^0) reacts with molecular oxygen (O_2) to form potassium superoxide (KO_2). This PPF compound continues to react with residual K^0 and converts to the highly sensitive potassium peroxide (K_2O_2) species.



(c) Peroxide Prevention

Since only the introduction of O₂ to the PPF compound will initiate the peroxide generation, storage of all PPF compounds should be under an inert atmosphere. When this is not practical, storage in a metal flammable cabinet that prevents light exposure has been offered as an acceptable alternative. Dry packed bottles (for example, Sigma Aldrich Sure/Seal™ bottles) stored in these cabinets leak over time thereby enabling the formation of PYDs. Required testing is in place to mitigate high PYD concentrations. Contrary to standard lore that low temperature storage may reduce peroxide formation,⁴ it is *not* advisable to store peroxide formers in refrigerators. There is no evidence that cold storage prevents or retards peroxide formation and in fact may lead to increased concentration of peroxides with disastrous results due to reduced peroxide solubility resulting in crystal formation.^{4,6}

Peroxide formation is also inhibited by the manufacturer via introduction of free radical scavengers (i.e., hydroquinone or diphenylamine, 2,6-ditert-butyl-p-methylphenol, polyhydrophenols, aminophenols, and arylamines) into the liquid PPF compound (i.e., tetrahydrofuran (THF) is typically stabilized with BHT).⁵ It should be noted that some inhibitors, phenolic inhibitors for instance, require the presence of oxygen in order to generate peroxyradicals (ROO·). Phenolic inhibitors react rapidly and selectively with peroxyradicals to isolate the radical.⁷ The free radical scavengers are effective inhibitors due to resonance stability and steric hindrance.

The best practice to ensure that any PPF compounds obtained do not become PYD species is to avoid prolonged storage via rapid (as possible) use. Once received the best methods for preventing dangerous levels of peroxide formation are to actively monitor and as required dispose (including unopened bottles) of PPF compounds.

(d) Peroxide Monitoring

As per Industrial Hygiene documentation (e.g., ESH 100.2.IH.4 requirements and Guidelines for Peroxidizable Organic Chemicals), upon receipt of any PPF chemical, bottles are labeled (see Figure 1), dated, and tested on a 6 month schedule after opening. Opened containers of liquid PPF chemicals should be tested after:

Class A: once opened and every 3 months, until emptied or disposed.

Class B: once opened and every 6 months, until emptied or disposed.

Class C: once opened and every 6 months, until emptied or disposed.

Prior to testing, use a flashlight to inspect the chemical containers for discoloration, crystallization, or liquid stratification, before any further interaction with the container. It is of note that crystallization does NOT always mean peroxides have been formed. If any of the above is observed, and/or the PPF chemical is suspected as having turned into a PYD species:

1. immediately limit access to the suspect container and clearly mark the container (without touching the container) indicating that the container should not be used or even moved by unauthorized personnel. This is

especially important if peroxide crystals or solid contamination are identified through visual inspection.

2. remove other chemicals from the area in which the suspected problem container is located *only* if this can be done without moving or disturbing the suspect container. Make sure that all chemical handlers working in the area are aware of the container, and the potentially explosive nature of the chemical.
3. contact your ES&H Coordinator or Environmental Compliance Coordinator.

(e) Safe Handling and Disposal Requirements

For safe handling, the peroxide concentration in PYD chemicals must be below 30 ppm (which is likely to change to > 50 ppm by Industrial Hygiene), as determined by SNL (ESH 100.2.IH.4). This limit is based on the limits of peroxide testing strips, and the Veolia requirement of less than 80 ppm. Veolia is a waste services company that aides in safe waste management, compliance, and efficient operating processes.⁸ The Hazardous Waste Handling Facility is a customer of Veolia.

The Hazardous Waste Handling Facility can only accept PPF/PYD compounds declared waste that adhere to the following:

1. a test-strip reading below 50 ppm (*vide infra*),
2. the observed reading included on the Waste Description and Disposal Request (WDDR),
3. coordination with hazardous waste disposal personnel concerning the peroxide ppm levels,
4. if neutralized, the container must be labeled as “NEUTRALIZED” prior to use or disposal (*note*: when the NEUTRALIZED PPF compound is no longer of use and scheduled for disposal, the additives and low pH must be included on the WDDR). For neutralization techniques see the ‘Methodology to Neutralize PYD Chemicals’ section.

(f) Peroxide Identification

The identification of peroxide levels in PPF/PYD compounds is conveniently determined by a variety of commercially available test-strips. All test-strips utilize a dip sample followed by a color change on the test pad after a set time frame. There is some disagreement on the storage of the test strips; however, in general it is agreed that the peroxide test strips should be stored at room temperature with their caps securely closed to prevent reaction with ambient moisture and light. Most manufacturers also advise closing the tube containing the test strips immediately after use. The test strips are also sensitive to other oxidizing agents such as free chlorine.

with a drop of distilled water. The test time as stated on the bottle label and in the catalogue is listed as 30 seconds.

The current (FY 2013) peroxide testing method used by the Hazardous Waste Handling Facility is to dip a new peroxide test strip into PPF solutions and briefly fan in air. The test pad is then lightly sprayed with deionized water. This test is performed in light and the color change is assessed at 1 minute.

(h) Aqueous H₂O₂ Identification

Four commercially available peroxide testing strips were used to test formulated hydrogen peroxide concentrations in water (Table 2). Figures 3-5 are pictures of the test strips based on the parameters of Table 2. For these experiments the test strips were submerged into freshly prepared aqueous hydrogen peroxide solutions, misted with deionized water, and recorded after 30 seconds elapsed (see section g for recommended testing procedure). All tests were performed under standard fluorescent light in a hood. Some correlation between the test strip and the bottle’s color palette were observed.

Table 2 Conditions for example peroxide test strip preparation.^a

Sample Number	Strip Type	ppm	μL of H ₂ O ₂ in 100mL of H ₂ O
1	WaterWorks™ 480014	blank	-
2	MQuant™ 1.10081.0001	blank	-
3	XploSens PS	blank	-
4	MQuant™ 1.10337.0001	blank	-
5	WaterWorks™ 480014	10	3.00
6	MQuant™ 1.10081.0001	10	3.00
7	WaterWorks™ 480014	50	15.01
8	XploSens PS	50	15.01
9	WaterWorks™ 480014	100	30.03
10	MQuant™ 1.10081.0001	100	30.03
11	XploSens PS	100	30.03
12	MQuant™ 1.10337.0001	100	30.03
13	XploSens PS	499	150.15
14	MQuant™ 1.10337.0001	997	300.30

^aUnless otherwise noted pictures were taken after 30 seconds.



Figure 3 Blank WaterWorks™ (1), MQuant™ 1.10081.0001 (2), XploSens PS (3), and MQuant™ 1.10337.0001 (4) test strips.



Figure 4 WaterWorks™ (5) and MQuant™ 1.10081.0001 (6) at 10 ppm (left), WaterWorks™ (7) and XploSens PS (8) at 50 ppm (middle), and WaterWorks™ (9), MQuant™ 1.10081.0001 (10), XploSens PS (11) at 100 ppm, and MQuant™ 1.10337.0001 at 100 ppm (right).



Figure 5 XploSens PS at 499 ppm (left) and MQuant™ 1.10337.0001 at 997 ppm (right).

Figure 6 shows the experimental results observed for each of the calculated concentrations. As expected, a darker color was noted as peroxide concentration increased. The top test pad for the MQuant™ 1.10337.0001 strip will change color when high peroxide concentration (~2000 ppm H₂O₂) is present. The strip was incorrectly suggestive of ~2000 ppm peroxide concentrations for test strips 12 (100 ppm) and 14 (997 ppm). The color palette on the XploSens PS bottle makes individual test strip identification difficult. Analysis for these strips is made easier when viewed as a series; however, strip 13 (500 ppm) is much darker than the bottle's 500 ppm reference. The other MQuant™ test strips (1.10081.0001) demonstrated a decisive progression of peroxide concentration. The results are not as definitive as the bottle indicates at 30 seconds. The manufacturer addresses this issue by stating coloration within three minutes can be interpreted as a positive result. Based on the totality of the aqueous test strip evaluation, the WaterWorks™ strips had the best correlation between strip and bottle even though some green coloration is observed.

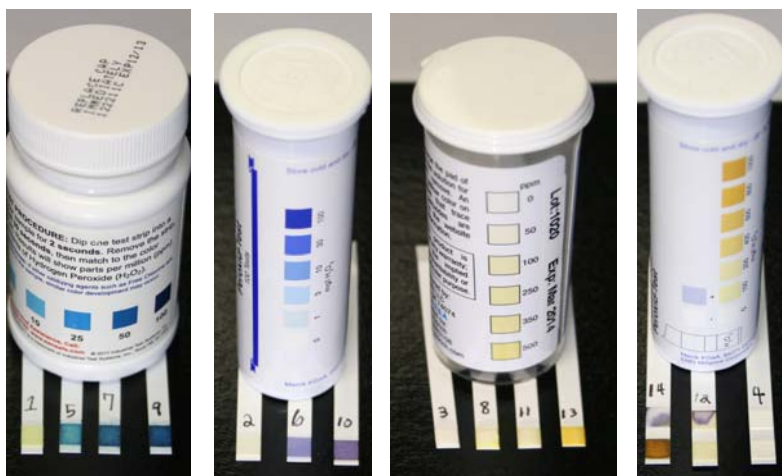


Figure 6 Combined WaterWorks™ test strips (left), Combined MQuant™ 1.10081.0001 test strips (left middle), Combined XploSens PS test strips (right middle), and Combined MQuant™ 1.10337.0001 test strips (right) after all testing was completed.

Figures 7-10 are used to demonstrate changes to strips over time and if strips dipped in deionized water test positive over time. The WaterWorks™ strips develop a deep green over time and they were the only strips to develop a color from water submersion. No observable changes were visible in the MQuant™ 1.10081.0001 test strips. Both the MQuant™ 1.10337.0001 and XploSens PS strips faded in color over time.

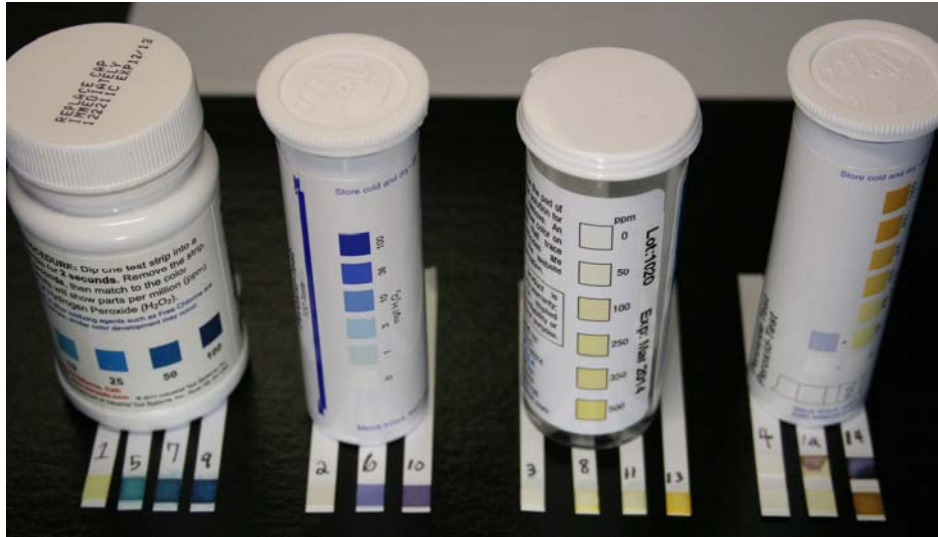


Figure 7 Peroxide test strips after all testing was completed.

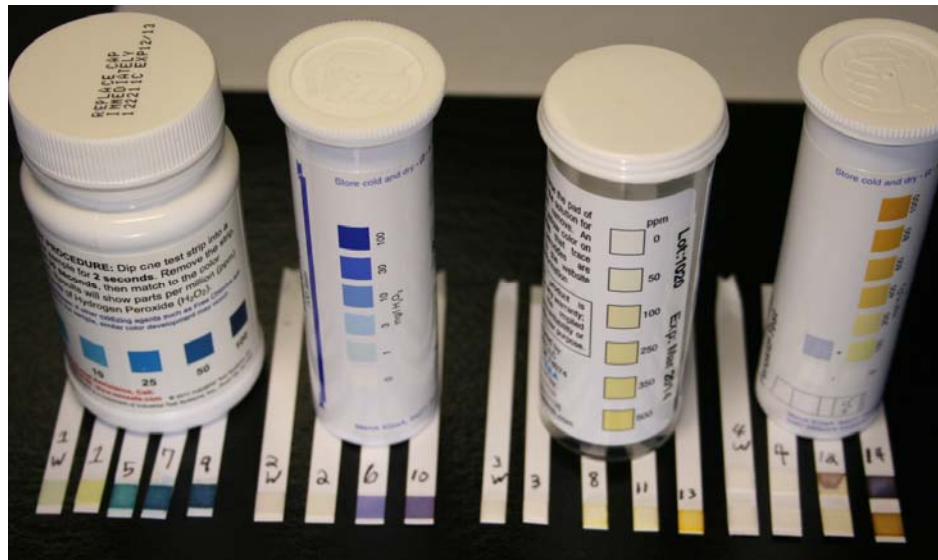


Figure 8 Peroxide test strips with additional blanks immersed in water (labeled with corresponding number and W) after all testing was completed.



Figure 9 Peroxide test strips with additional blanks immersed in water (labeled with corresponding number and W) 24 hours later.



Figure 10 Peroxide test strips with additional blanks immersed in water (labeled with corresponding number and W) 96 hours after immersion in water.

(i) Organic peroxide in THF Identification

A set of calculated peroxide containing solutions (10, 50, 100, 500, and 1000 ppm) were investigated replacing water with the model solvent THF. Three organic peroxides (Figure 11) were used as the contaminant: (a) 2-hydroperoxy-2-methylpropane (**A**), (b) 2-hydroxyperoxy-2-((2-hydroperoxybutan-2-yl)peroxy)butane (**B**), and (c) 3,3'-peroxybis(pentane-2,4-dione) (**C**). All peroxide solutions were first observed to be miscible (1:1) with THF. The parameters used to obtain the peroxide concentrations are given in Table 3. It should be noted that **B** has three peroxides in its structure. Therefore column **D** in Table 3 is the normalized value. After submerging the test strip in the respective solution, it was fanned in a fume hood for 15 seconds, misted with water, and the color was recorded after 1 minute (as noted in section g). Again all tests were performed under standard fluorescent light in a hood.

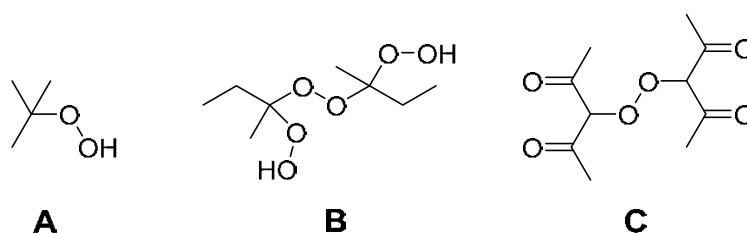


Figure 11 Depiction of (A) 2-hydroperoxy-2-methylpropane, (B) 2-hydroxyperoxy-2-((2-hydroperoxybutan-2-yl)peroxy)butane, and (C) 3,3'-peroxybis(pentane-2,4-dione).

Table 3 Conditions for organic peroxide test strip comparison.^a

ppm	A ^b	B ^c	C ^d	D ^e
10 ^f	1 (2.2 μL)	16 (2.9 μL)	31 (2.7 μL)	46 (0.9 μL)
10 ^g	2 (2.2 μL)	17 (2.9 μL)	32 (2.7 μL)	47 (0.9 μL)
10 ^h	3 (2.2 μL)	18 (2.9 μL)	33 (2.7 μL)	48 (0.9 μL)
10 ⁱ	4 (2.2 μL)	19 (2.9 μL)	34 (2.7 μL)	49 (0.9 μL)
50 ^f	5 (11.1 μL)	20 (14.3 μL)	35 (13.8 μL)	50 (4.8 μL)
50 ^g	6 (11.1 μL)	21 (14.3 μL)	36 (13.8 μL)	51 (4.8 μL)
50 ^h	7 (11.1 μL)	22 (14.3 μL)	37 (13.8 μL)	52 (4.8 μL)
50 ⁱ	8 (11.1 μL)	23 (14.3 μL)	38 (13.8 μL)	53 (4.8 μL)
100 ^f	9 (22.2 μL)	24 (28.6 μL)	39 (27.5 μL)	54 (9.5 μL)
100 ^g	10 (22.2 μL)	25 (28.6 μL)	40 (27.5 μL)	55 (9.5 μL)
100 ^h	11 (22.2 μL)	26 (28.6 μL)	41 (27.5 μL)	56 (9.5 μL)
100 ⁱ	12 (22.2 μL)	27 (28.6 μL)	42 (27.5 μL)	57 (9.5 μL)
500 ^h	13 (111.1 μL)	28 (143 μL)	43 (138.0 μL)	58 (47.7 μL)
500 ⁱ	14 (111.1 μL)	29 (143 μL)	44 (138.0 μL)	59 (47.7 μL)
1000 ⁱ	15 (222.59 μL)	30 (286.6 μL)	45 (276.2 μL)	60 (95.5 μL)

^aCommercially available peroxides used: 25 mL of 5-6 M tert-butyl hydroperoxide (**A**, CAS number 75-91-2) with a calculated (5M) stock peroxide concentration of 450600 ppm, 100 mL of ~35 wt. % 2-butanone peroxide solution (**B**, CAS number 1338-23-4) with a stock peroxide concentration of 350000 ppm, 500 mL of ~34 wt. % 2,4-pentanedione peroxide solution (**C**, CAS number 37187-22-7) with a stock peroxide concentration of 363120 ppm. All peroxides were observed to be soluble (1:1) in Tetrahydrofuran (inhibitor-free, CHROMASOLV[®] Plus, for HPLC, ≥99.9%, CAS number 109-99-9). ^bPeroxide test strip number (volume of stock **A** added to 100 mL of THF in parentheses). ^cPeroxide test strip number (volume of stock **B** added to 100 mL of THF in parenthesis). ^dPeroxide test strip number (volume of stock **C** added to THF in parentheses). ^e**B** normalized by dividing volume by three (volume of stock **B** added to 100 mL of THF in parenthesis). ^fWaterWorks[™] 480014 test strip. ^gMQuant[™] 1.10081.0001 test strip. ^hXploSens PS test strip. ⁱMQuant[™] 1.10337.0001 test strip.

Figures 12-17 are pictures of the resulting test strips utilizing A. No significant coloration was observed for any of the MQuant™ 1.10337.0001 test strips. Both the WaterWorks™ and MQuant™ 1.10081.0001 test strips yielded positive results; however, the colors noted were found to be significantly lower than actual values. The XploSens PS strips were the only ones to yield a distinct gradual coloration with the concentrations analyzed. Again, the color palette on the XploSens PS bottle makes individual test strip identification difficult.



Figure 12 Test strips (1-4) of A with a peroxide concentration of 10 ppm.



Figure 13 Test strips (5-8) of A with a peroxide concentration of 50 ppm.

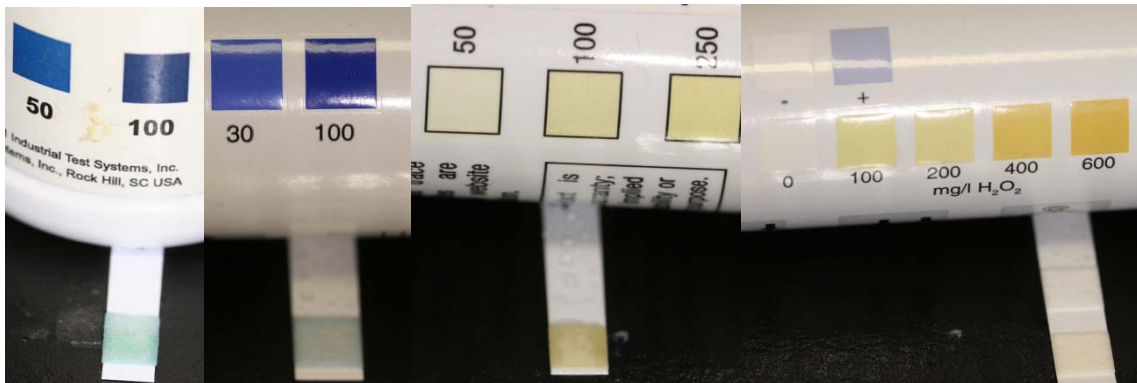


Figure 14 Test strips (9-12) of A with a peroxide concentration of 100 ppm.

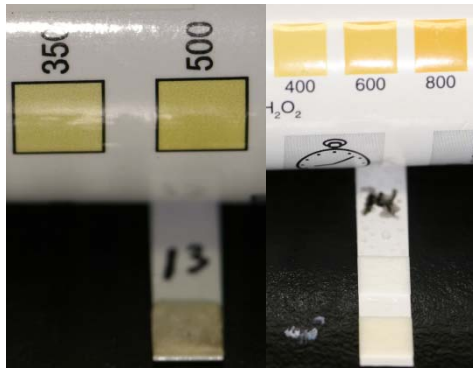


Figure 15 Test strips (13-14) of A with a peroxide concentration of 500 ppm.



Figure 16 Test strip (15) of A with a peroxide concentration of 1000 ppm.

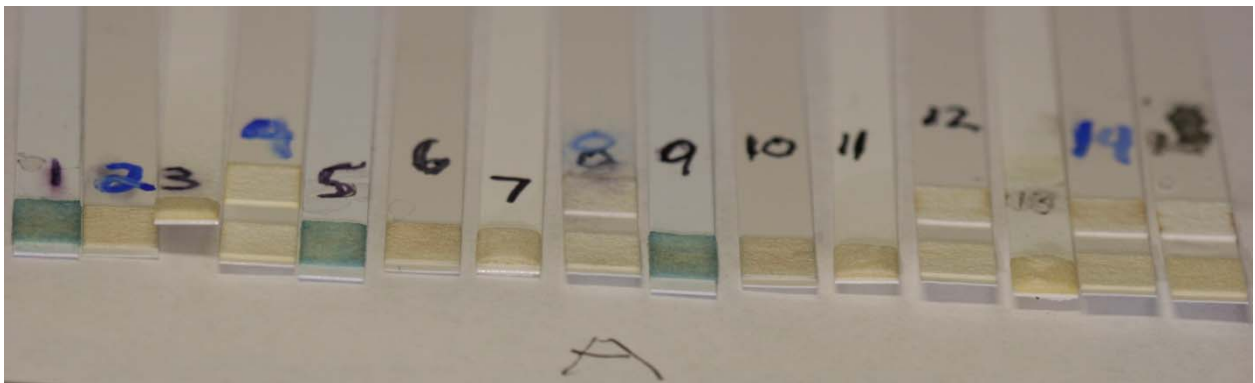


Figure 17 Test strips (1-15) of A after testing complete.

Figures 18-25 are pictures of the resulting test strips utilizing **B**. All strips successfully identified the presence of peroxides and all exhibited a gradual increase as concentration increased.

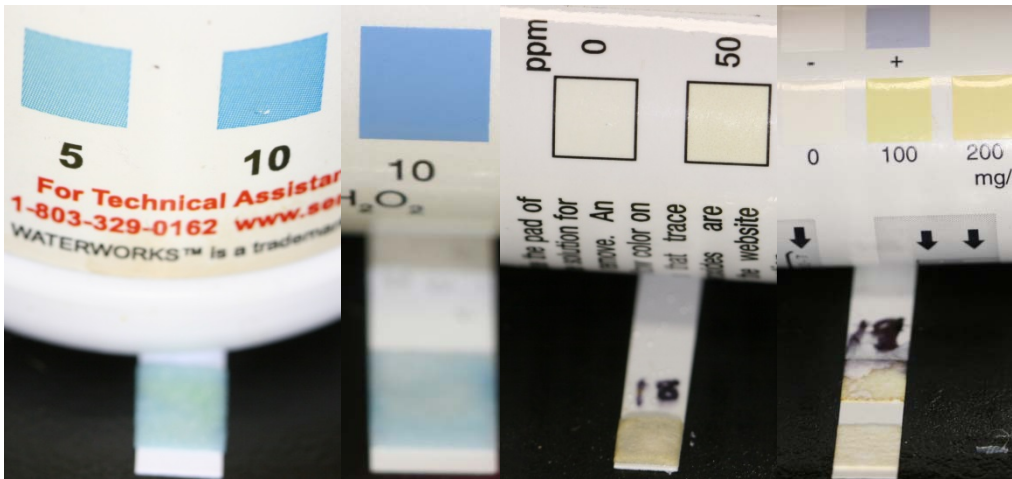


Figure 18 Test strips (16-19) of B with a peroxide concentration of 10 ppm.

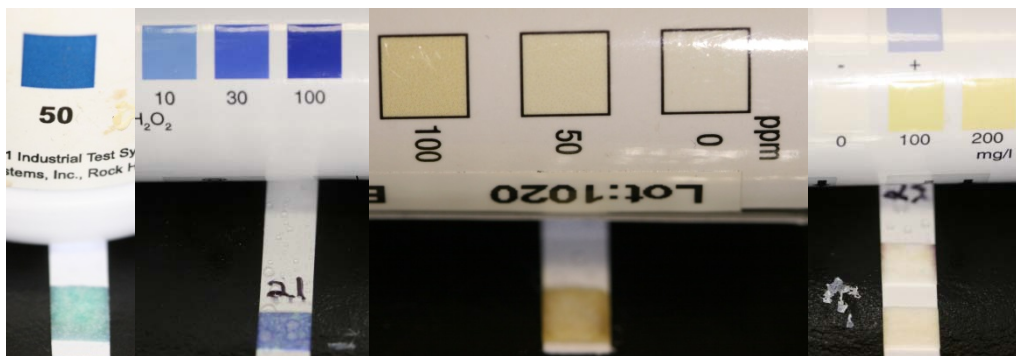


Figure 19 Test strips (20-23) of B with a peroxide concentration of 50 ppm.



Figure 20 Test strips (24-27) of B with a peroxide concentration of 100 ppm.

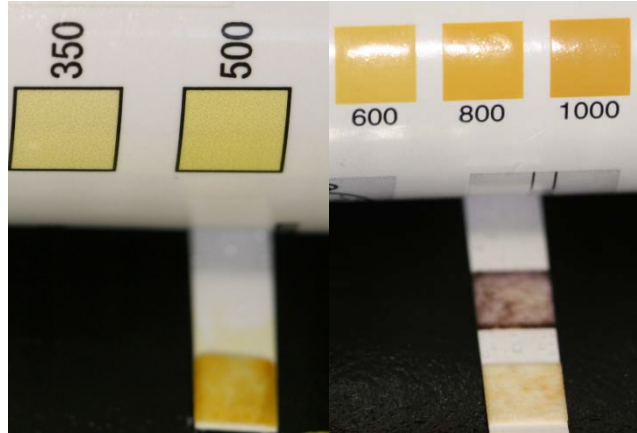


Figure 21 Test strips (28-29) of B with a peroxide concentration of 500 ppm.



Figure 22 Test strip (30) of B with a peroxide concentration of 1000 ppm.

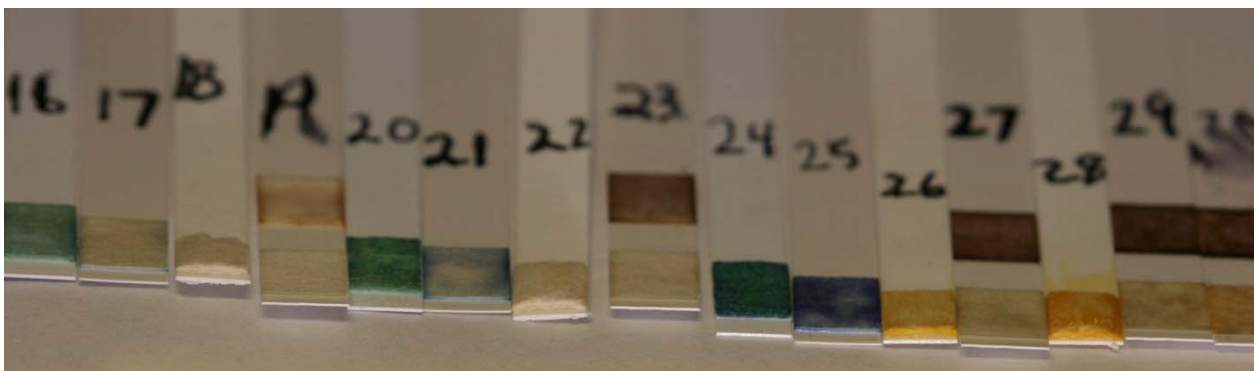


Figure 23 Test strips (16-30) of B after testing complete.

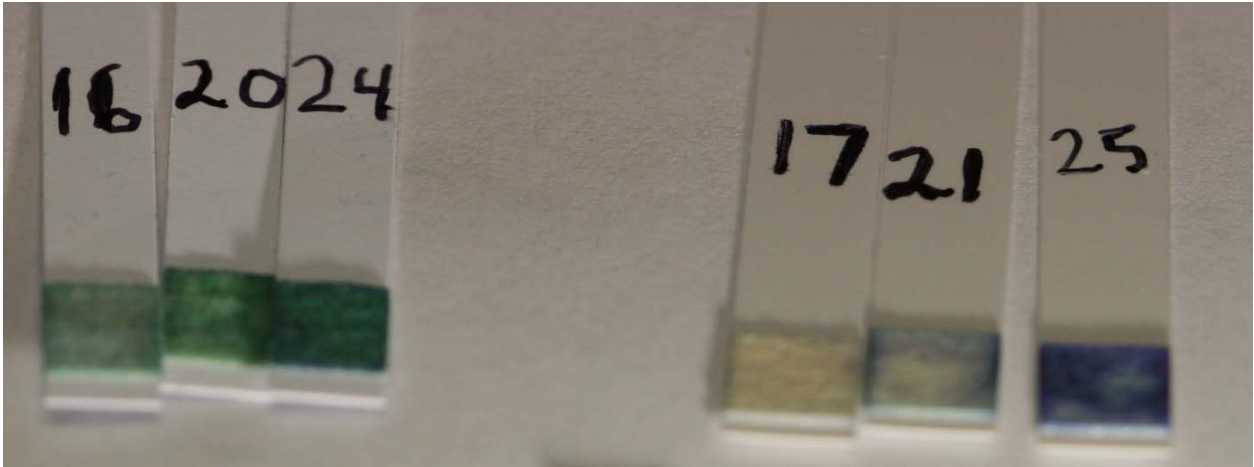


Figure 24 WaterWorks™ (left) and MQuant™ (right) test strips of B after testing complete.

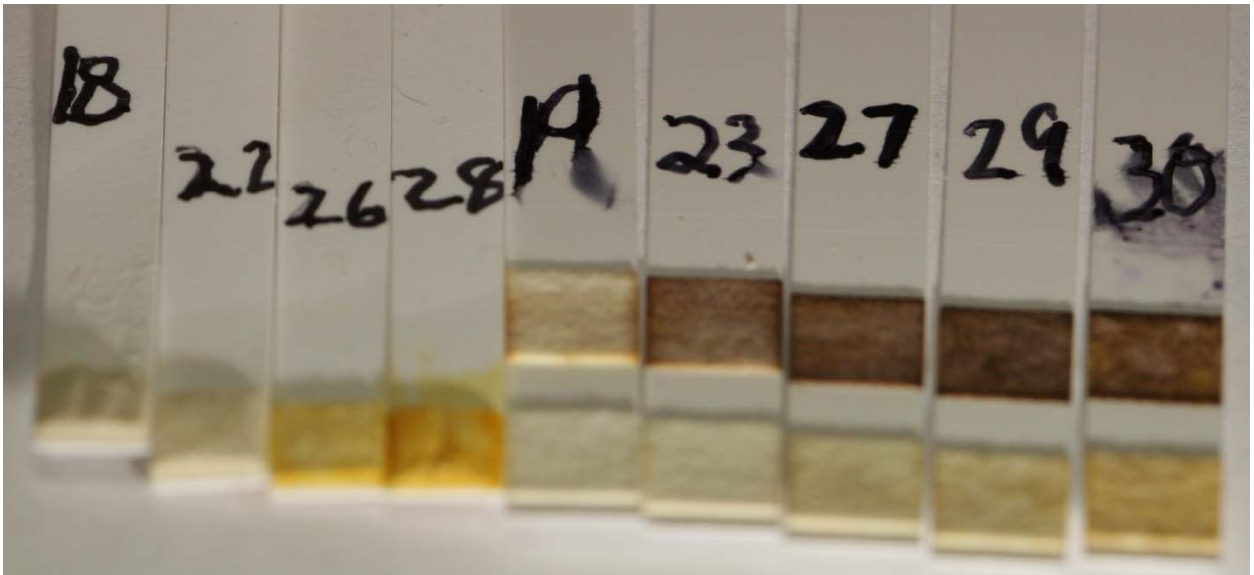


Figure 25 XploSens PS (left) and MQuant™ (right) test strips of B after testing complete.

Figures 26-33 are pictures of the resulting test strips utilizing C. With the exception of the MQuant™ 1.10337.0001 test strips, peroxide concentrations were successfully identified and in general a gradual increase as concentration increased was observed.

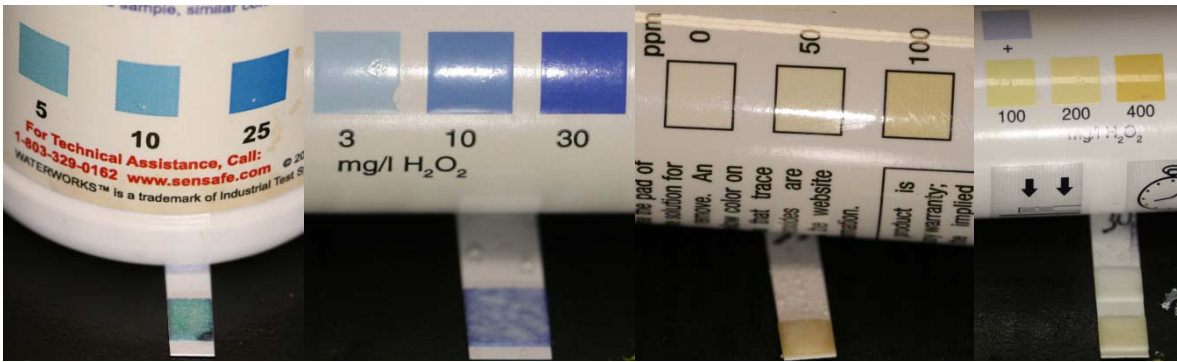


Figure 26 Test strips (31-34) of C with a peroxide concentration of 10 ppm.

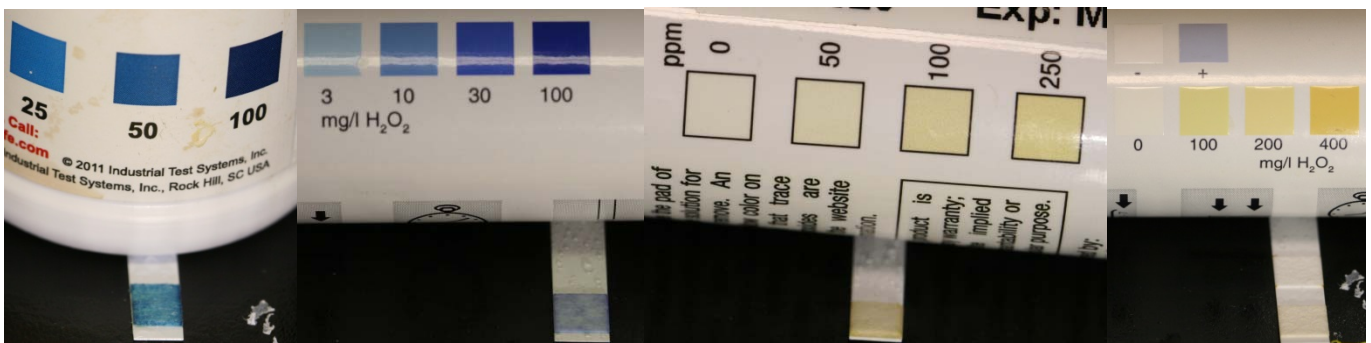


Figure 27 Test strips (35-38) of C with a peroxide concentration of 50 ppm.

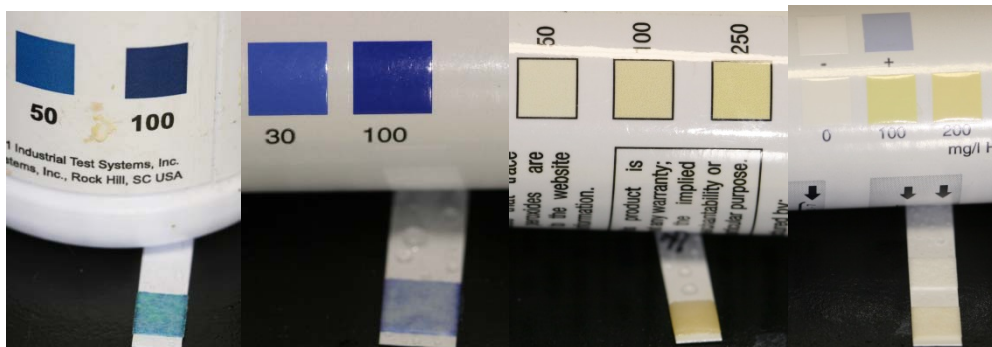


Figure 28 Test strips (39-42) of C with a peroxide concentration of 100 ppm.

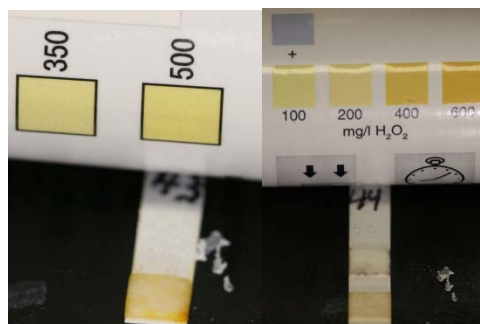


Figure 29 Test strips (43-44) of C with a peroxide concentration of 500 ppm.

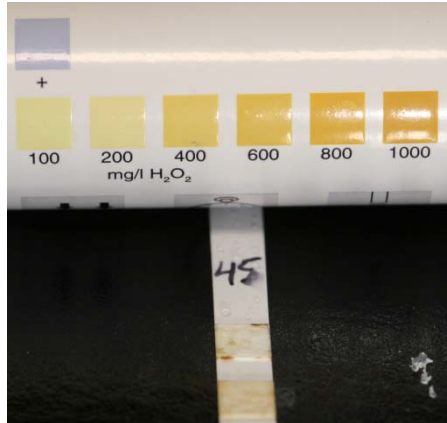


Figure 30 Test strip (45) of C with a peroxide concentration of 1000 ppm.

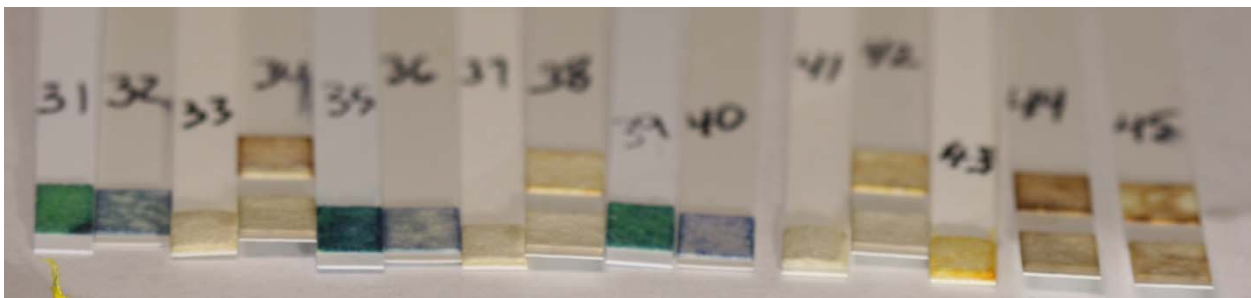


Figure 31 Test strips (31-45) of C after testing complete.

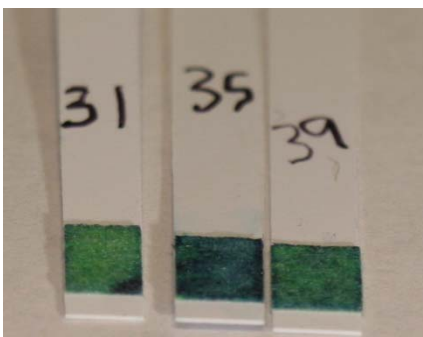


Figure 32 WaterWorks™ test strips of C after testing complete.

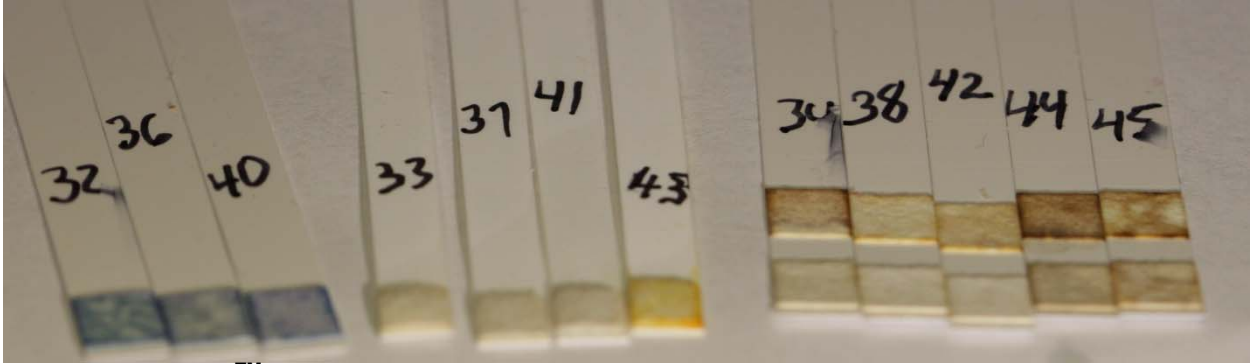


Figure 33 MQuant™ (left and right) and XploSens PS (Middle) test strips of C after testing complete.

Figures 34-41 are pictures of the resulting test strips utilizing normalized values of B. Again, all strips successfully identified the presence of peroxides and all exhibited a gradual increase as concentration increased. Over time the second pad on the MQuant™ 1.10337.0001 test strip was incorrectly positive.

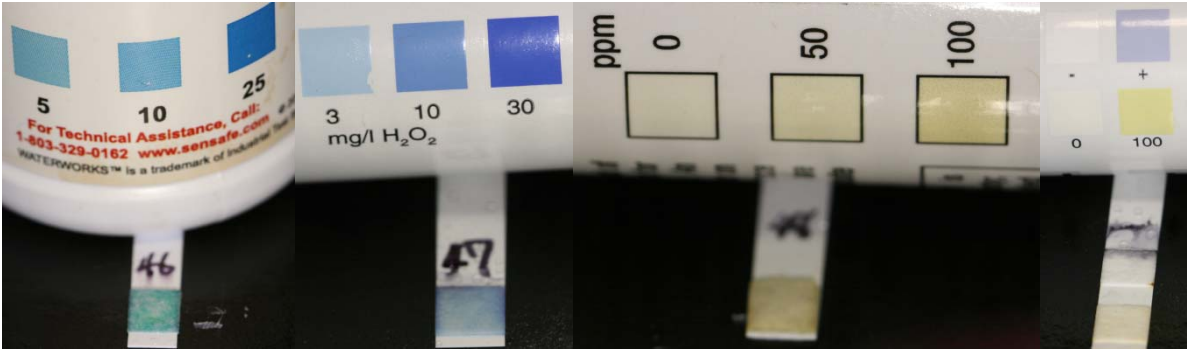


Figure 34 Test strips (46-49) of D (B normalized) with a peroxide concentration of 10 ppm.



Figure 35 Test strips (50-53) of D (B normalized) with a peroxide concentration of 50 ppm.

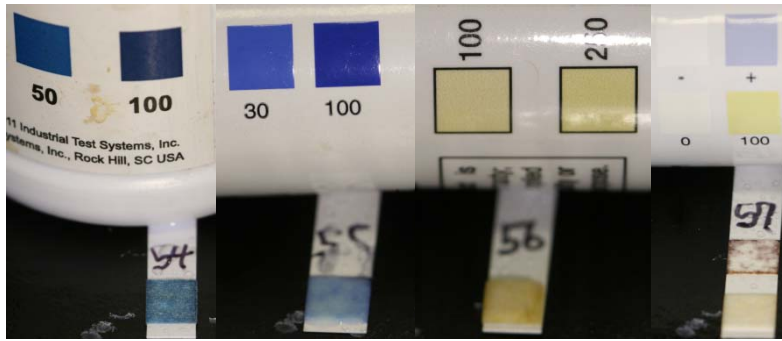


Figure 36 Test strips (54-57) of D (B normalized) with a peroxide concentration of 100 ppm.

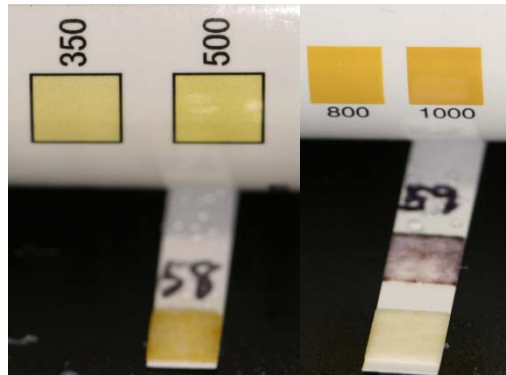


Figure 37 Test strips (58-59) of D (B normalized) with a peroxide concentration of 500 ppm.

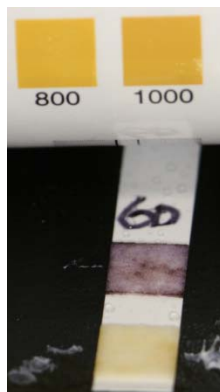


Figure 38 Test strip (60) of D (B normalized) with a peroxide concentration of 1000 ppm.

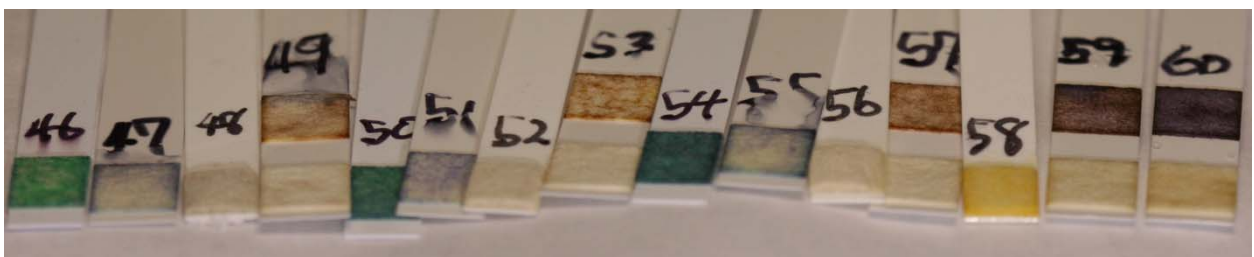


Figure 39 Test strips (16-30) of D (B normalized) after testing complete.

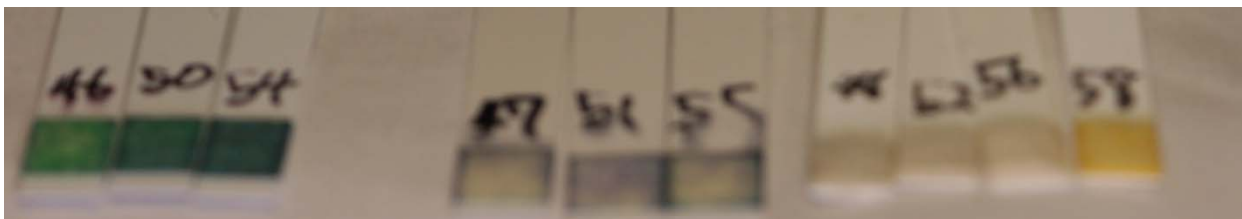


Figure 40 WaterWorks™ (left), MQuant™ (middle), and XploSens PS (right) test strips of D (B normalized) after testing complete.

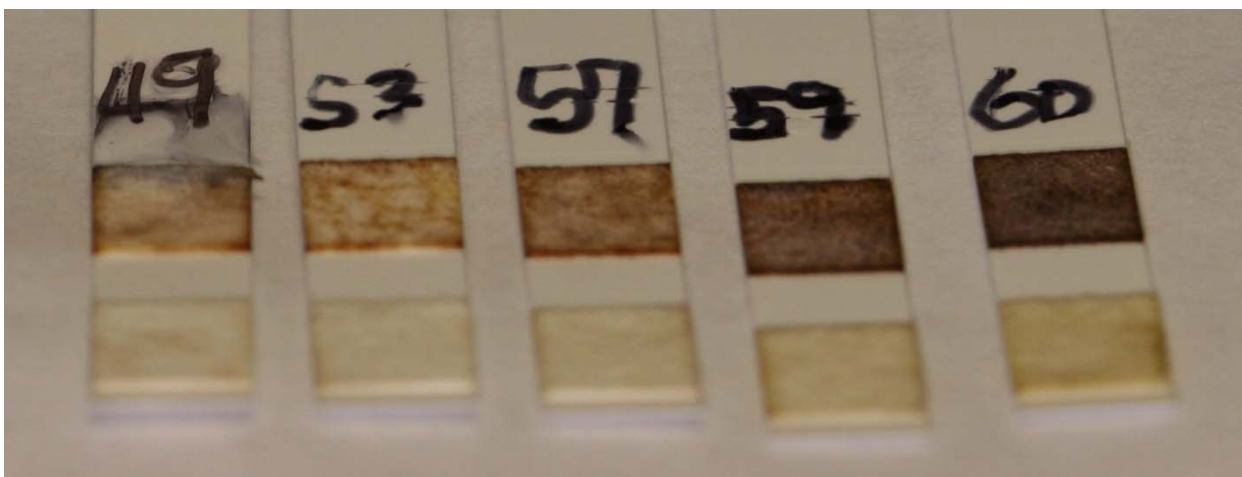


Figure 41 MQuant™ test strips of D (B normalized) after testing complete.

Differences between the contaminant **B** and **D** were observed until the 100 ppm concentration was tested. The WaterWorks™, MQuant™ 1.10081.0001, and XploSens PS test strips successfully identified the presence of peroxides at all of the concentrations studied. The XploSens PS test strip successfully identified all of the peroxide concentrations; however, as mentioned above single strip analysis is difficult do due to slight variations in the color palette. Unfortunately, a liquid cyclic peroxide was not commercially available for this analysis. Based on the inability to identify hydroperoxides coupled with the identification of peroxides in old THF bottles, it is presumed that the strips successfully identify the presence of cyclic peroxides.

(j) Peroxide Neutralization

If a test strip reads ≥ 30 ppm (likely to change to > 50 ppm), the material should be neutralized for safe handling. Neutralization techniques are detailed in the methodology to neutralize PYD chemicals section.

2. BACKGROUND

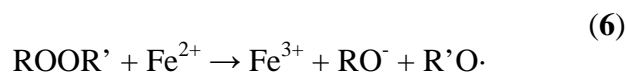
(a) Peroxide Neutralization Chemistry

Current peroxide neutralization involves the use of a Co(II)⁹, Fe(II)^{1,2,4,10} or [Mo₂O₅(OH)]¹¹ reagent. The Co(II) and Fe(II) neutralizers were chosen based on their ability to readily oxidize in the presence of peroxide materials. Of these neutralizers, the Co(II) precursor is used when a slow (≤ 30 days) reaction is necessary engendering a safe, room temperature route. The Fe(II) precursor possesses a stronger oxidation potential in acidic aqueous solutions and thus a more rapid conversion can occur; however, some elevation of the sample's temperature must be endured during the neutralization process. An acidic solution is required as alkaline solutions convert hydrated ferrous complexes to colloidal ferric complexes which inhibit neutralization.¹² In contrast to the M(II) reagents, the [Mo₂O₅(OH)] complex was selected based on its electronic transport and acidic properties,¹¹ which allows for rapid conversion of peroxides to alcohols. A quick review of the neutralization reactions that occurs for each of these routes are presented below.

(b) Oxidation

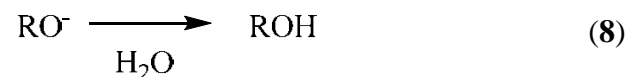
Typically an iron(II) (or Fe^{2+}) salt (sulfate or chloride) is mixed with concentrated sulfuric acid (H_2SO_4) and water (H_2O).¹³ In most instances, the precursor of choice has been $\text{Fe}(\text{SO}_4)\cdot 7\text{H}_2\text{O}$. It is of note that the monohydrate derivative is not as efficient at neutralization, which is believed to be due to discrepancies in the concentration levels of the Fe^{2+} in water (i.e., the hepta hydrate allows for more Fe^{2+} to be solubilized versus the monohydrate). The process of neutralization is in dispute but two pathways have been proposed: (i) radical process *versus* (ii) oxoiron (IV) complex formation.

(i) *Radical Process*. For the radical process mechanism, once the Fe^{2+} is generated in solution, it is then added to the peroxide containing chemical. As depicted in Equations 6 and 7, the Fe^{2+} method proceeds via a radical process.^{14,15} In this process the peroxide reacts with the Fe^{2+} to form the Fe^{3+} cation, along with an alkoxy anion (OR'^-) and alkoxy free radical ($\text{RO}\cdot$). The $\text{RO}\cdot$ reacts with the remaining Fe^{2+} cation to generate more Fe^{3+} and OR'^- . This continues until the peroxide is consumed.



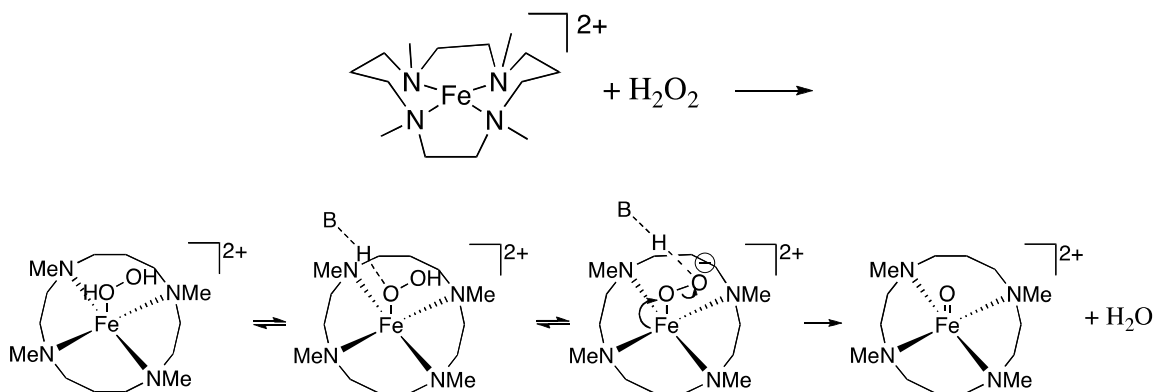
R = H or organic, R' = H or organic

The fate of the OR'^- is the eventual formation of an alcohol or water (equation 8).



R = H or organic

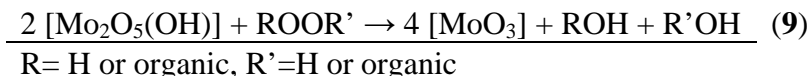
(ii) *Oxoiron (IV)*. For this mechanism, an oxoiron (IV) complex is proposed as the critical intermediate. This process is supported by a kinetic reinvestigation of whether or not O_2 is evolved and the resulting alteration to Fe^{3+} concentrations¹⁶, DFT studies¹⁷, and *in situ* oxoiron (IV) complex production.¹⁸ The intermediate is generated from the addition of hydrogen peroxide to a Fe^{2+} complex. UV-Vis spectra of this combination can be used to monitor the formation of an oxoiron (IV) complex. The mechanism is essentially a base catalyzed oxidative addition (Scheme 1). The mechanism is initiated by coordination of hydrogen peroxide to the iron (II) complex. The base deprotonates the coordinated peroxide resulting in oxidative addition of oxygen to generate an oxoiron (IV) complex.



Scheme 1. Mechanism of oxoiron (IV) complex synthesis.

(c) $\text{Mo}_2\text{O}_5(\text{OH})$

The reaction of $[\text{Mo}_2\text{O}_5(\text{OH})]$ with peroxides is shown below in equation 9. The Mo-reagent undergoes a rapid reaction with the peroxide to yield water and/or alcohols (Equation 9).



There are several benefits of the $[\text{Mo}_2\text{O}_5(\text{OH})]$ neutralization process, including a color indication for successful neutralization. A yellow precipitate is indicative of the formation of peroxy complexes of Mo, a direct result of high peroxide concentrations.¹¹ $[\text{Mo}_2\text{O}_5(\text{OH})]$ can also be used for peroxide test strips by air drying a $[\text{Mo}_2\text{O}_5(\text{OH})]$ /butanol solution on filter paper. Unfortunately, this process is not as efficient and is also significantly more costly than the Fe^{2+} method (vide infra).

3. METHODOLOGY TO NEUTRALIZE PYD CHEMICALS

Outlined below is the methodology suggested to SAFELY neutralize PPF chemicals that are above the safe handling limit (i.e., PYD) but do not exceed the Industrial Hygiene recommended limit of 800 ppm. If levels above 800 ppm are observed, dilution is a viable method to reduce concentration in order to allow for neutralization. This practice necessitates the buddy system (the presence of another qualified MOW). Additionally, management, ES&H, and IH should be involved in any PYD systems identified to have formed unacceptable peroxide levels. If you are not familiar or comfortable with any of the described procedures, it is recommended that you seek additional help from more experienced coworkers.

(a) Neutralization Process for Chemical Management^{II,III}

Once a PPF chemical has been identified as a PYD (concentration level between 51 - 800 ppm)^{IV} and a management approved neutralization plan has been developed then:

1. Notify management, nearby labs, and ES&H personnel as to the schedule of the neutralization process.
2. Verify a qualified laboratory assistant is available, able, and willing to assist.
3. Ensure fire mitigation equipment (i.e., fire extinguisher) is available.
Note: peroxide fires are difficult to extinguish.
4. Ensure a cleared fume hood, a temperature monitoring device (i.e., thermometer or thermocouple), and an ice bath are available.
5. Locate clean and proper glassware (PyrexTM or equivalent and at least twice the volume to be treated) including: (i) **Neutralization Flask A** - a 2 L or larger flask with a stir bar and (ii) **Neutralization Solution Flask B** – a 2 L or larger flask with a stir bar.
6. Limit volume of peroxide yielded derivative (PYD) chemical to be neutralized to 1 liter or less per reaction. Use extreme care when handling chemical bottles, minimizing bumping, mixing, shaking, etc.
7. Place the 2 L **Neutralization Flask A** in an ice bath.
8. Using secondary containment carefully transfer less than 1 liter of the PYD chemical to be neutralized into the **Neutralization Flask A**.
9. In the **Neutralization Solution Flask B** add, in order, 110 mL of H₂O, 6 mL concentrated sulfuric acid, and 110 g of iron sulfate heptahydrate (Fe(SO₄)•7H₂O).
10. Allow the **Neutralization Solution B** mixture to stir for 5 minutes.
11. Add **Neutralization Solution B** mixture to the cooled PYD chemical in the **Neutralization Flask A** and stir.
12. Monitor the temperature of the reaction in **Neutralization Flask A**. Once the temperature no longer increases, the reaction is complete. The neutralization is a rapid process and can be tested within a couple minutes.
13. Retest^V the solution in **Neutralization Flask A** for peroxide concentration levels by dipping a new peroxide test strip into neutralized product. Briefly fan in air and then lightly spray (mist) the strip with deionized (DI) water. Observe color change at 1 minute. Perform this test in light.
14. If needed repeat steps 9 – 13 until an acceptable peroxide strip reading occurs.
15. Label the **Neutralization Flask A** as “NEUTRALIZED”.

^{II} As of APR 2013: this process was successfully performed at Sandia by: Jeremiah Sears (1815), Mathias Celina (1819), Adam Pimentel (1819), Leah Appelhans (1835), Nicholas, Hudak (2546), Constantine Stewart (6823), and Michael Kent (8622)

^{III} For liquid solutions. Note that the Hazardous Waste Handling Facility can accept un-neutralized 30% H₂O₂ as waste.

^{IV} If above 800 ppm, dilution is a viable method to reduce concentration in order to neutralize.

^V The method described is currently (FY 2013) used by the Hazardous Waste Handling Facility.

(b) Dilution Example for Chemical Management^{VI}

For this example, consider a 4 L bottle of the PPF tetrahydrofuran (THF) that was found to contain a peroxide concentration of just less than 1000 ppm. This THF was declared a PYD and therefore neutralization is required. The concentration is too great to handle safely and dilution was decided as a mechanism to reduce the peroxide concentration.

The general equation that this follows is

$$M_1V_1 = M_2V_2$$

where M = concentration and V = volume

Once a high peroxide concentration in a PYD (> 800 ppm) chemical has been identified and a management approved dilution plan has been developed

1. Notify management, nearby labs, and ES&H personnel as to the schedule of the dilution process.
2. Verify a qualified laboratory assistant is available, able, and willing to assist.
3. Ensure fire mitigation equipment (i.e., fire extinguisher) is available.
Note: peroxide fires are difficult to extinguish.
4. Ensure a cleared fume hood is available.
5. Ensure the high concentration PYD THF (**THF-999**) is ready for dilution and that a PPF bottle of THF (**THF-0**)^{VII} is available at sufficient quantity to allow for the necessary dilution.
6. Locate clean and proper glassware (PyrexTM or equivalent and at least twice the volume to be treated) including: two 2 L or larger flasks.
7. Using secondary containment carefully transfer half of the 4 L bottle of **THF-999** to the empty 4 L flask (**A-1**).
8. Add 0.5 L of **THF-0** to **A-1**.
9. **A-1** now has a peroxide concentration of 799 ppm and can be safely neutralized in 1 L quantities (*vide supra*).
10. Using secondary containment carefully transfer the remainder of the 4 L bottle of **THF-999** to the second empty 4 L flask (**A-2**).
11. Add 0.5 L of **THF-0** to **A-2**.
12. **A-2** can now be safely neutralized in 1 L quantities (*vide supra*).

^{VI} Example dilution for 4 L of THF with a peroxide concentration of 999 ppm. Note a higher peroxide concentration requires more dilution.

^{VII} Peroxide concentration at 0 ppm.

(c) Neutralization Solution Preparation and Use

A description of the Neutralization process described above is detailed below. Initially concentrated sulfuric acid is added to water. After this, the iron sulfate heptahydrate is added slowly. The solution is vigorously stirred using a magnetic stir-bar and plate for a couple minutes (~ 5 min). The generation of iron (II) ions is exothermic as a change in temperature may be observed. Typically this change is ≤ 20 °C. After stirring, the light green solution in **Neutralization Solution Flask B** is added to the chemical containing peroxides in **Neutralization Flask A**. This is allowed to stir a couple minutes as well. The strip test is then used again to test for peroxide concentration.

Half quantities (55 g iron sulfate heptahydrate, 55 mL water, and 2.5 mL H₂SO₄) can successfully neutralize 2 L of THF.

It should be noted that relatively fresh iron sulfate monohydrate should be used for this process, since older iron sulfate monohydrate has been found to be unsuccessful in neutralization.

(d) Molybdenum Neutralization

Alternatively, [Mo₂O₅(OH)] can be prepared from refluxing 30 g of MoO₃, 300 mL of *n*-butanol, and 5 mL of concentrated HCl for 6 hours.¹¹ During this time a dark blue color should develop. The reaction is then cooled to room temperature, filtered, washed with *n*-butanol, and dried in a vacuum oven (25 °C). Yields of 98% are reported. The [Mo₂O₅(OH)] product can then be used to neutralize peroxide forming chemicals with the added benefit of color indication (yellow) in the presence of high concentrations of peroxides. It is advised that the chemical to be neutralized be placed in an ice bath. XPell™ R is a commercially available, patent pending product that neutralizes peroxides in a similar manner. XPell™ R can be purchased in 50 gram quantities but expires a year after purchase. The suggested ratio is 0.5 grams per liter of peroxide forming chemical. Be advised that much larger quantities may be required as this method is not as efficient as the iron sulfate method.

4. SUMMARY AND CONCLUSIONS

This report is in response to recent discoveries of chemicals with high peroxide concentrations. The WaterWorks™, MQuant™ 1.10081.0001, and XploSens PS test strips were successful at identifying the presence of both hydrogen and organic peroxides. The XploSens PS test strip successfully identified all of the peroxide concentrations; however, single strip analysis is difficult do due to slight variations in the color palette. The iron sulfate method is a superior technique for neutralizing chemicals that contain peroxides when dilution is not a practical method.

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APPENDIX A. PREVIOUS SAND REPORT ON PEROXIDE FORMING CHEMICALS



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SAND: 2011-3509 P



Chemical Laboratory Safety

INTERNATIONAL CHEMICAL THREAT REDUCTION DEPARTMENT

Peroxidizable Compounds

(May 9, 2011 – Version 1.01)

Research laboratories contain a wide variety of chemicals that can be potentially dangerous. Some of the common solvents used in synthetic or analytical labs can be flammable, irritants and toxic if used inappropriately. However, even when used safely some of these solvents and chemicals can develop into dangerous compounds over time by converting to peroxides and other potentially explosive compounds. This discussion, while not all inclusive of all the dangers associated with such compounds, gives the reader an introduction and some basic information on peroxidizable and potentially explosive compounds. The discussion is broken down into the following sections.

- I. What are peroxides?
- II. Compounds susceptible to peroxide formation and how they are formed
- III. Acceptable levels of peroxides
- IV. Styrene – auto polymerization
- V. Determination of peroxide levels
- VI. Neutralization of peroxides
- VII. References

I. What are peroxides?

Any compound containing an oxygen-oxygen single bond is called a peroxide. Furthermore peroxides can be classified as organic peroxides or inorganic peroxides. The oxygen-oxygen bond in these peroxide compounds is relatively unstable and will easily cleave into reactive radicals.

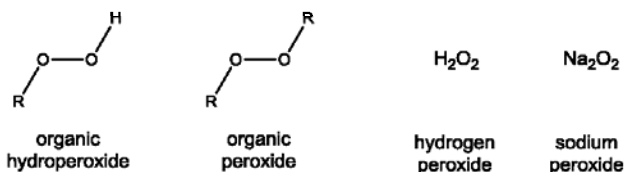


Figure 1. Types of Peroxides

APPENDIX A. Previous SAND report on peroxide forming chemicals.

II. Compounds susceptible to peroxide formation and how they are formed

Particular organic compounds are capable of undergoing auto-oxidation under mild conditions to form peroxides (<100 °C, UV light exposure (photoperoxidation) or by radical initiators). Ethers are normally identified as compounds that easily form peroxides but they are not the only compounds that do so. In general, any compound with an activated hydrogen atom or weak carbon-hydrogen bond can potentially form peroxides. Clark compiled a key to identify compounds with easily activated hydrogen atoms. These hydrogen atoms are found on certain types of carbon atoms and are illustrated by the following classes of compounds:[1]

Methylene groups (-CH₂-) adjacent to an ether oxygen (-CH₂-O-) such as diethyl ether (CH₃CH₂-O-CH₂CH₃), tetrahydrofuran, dioxane, diglyme.

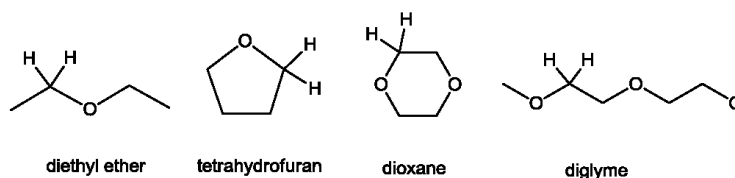


Figure 2. Typical ether solvents showing methylene hydrogen locations that are susceptible to peroxide formation.

Methylene groups attached to a vinyl group (C=C-CH₂) or a benzene ring, for example allyl compounds or benzyl compounds.

Methine group between two methylene groups (-CH₂-CH-CH₂-), for example iso-propyl compounds and decahydro-, naphthalenes.

Methine groups (-CH-) between two oxygen atoms, for example an acetal (O-CH-O).

Methine groups between a benzene ring and a methylene group (Ph-CH-CH₂), examples include cumene, and tetrahydronaphthalene.

Vinyl groups (-C=CH₂) vinyl compounds such as dienes, styrene and other olefinic type monomers.

Using diethyl ether as an example, the addition of oxygen into one of the weak methylene hydrogen bonds to form the peroxide is shown below in Figure 3. It would be of interest to know if the remaining hydrogen atom attached to the newly formed hydroperoxy carbon is susceptible to insertion of a second O₂. If this carbon-hydrogen bond is also prone to cleavage then this only makes a bad situation worse by further peroxidation of the ether thus making the molecule even more unstable and predisposed to detonation.

APPENDIX A. Previous SAND report on peroxide forming chemicals.

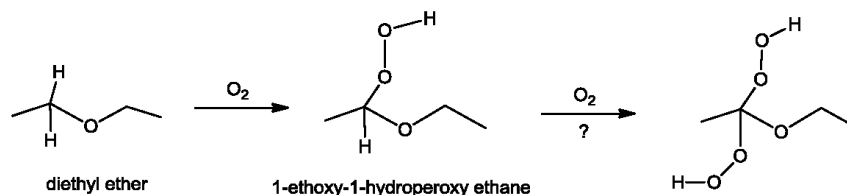


Figure 3. Route to the formation of peroxidized diethyl ether.

Clark also discusses oxygen content in the formation of peroxides. There is a direct correlation between the instability of a peroxide compound with an increase in oxygen content. A phenomenon called *oxygen balance* eventually comes into play. Oxygen balance has to do with the number of oxygen atoms in the peroxide compound and is related to combustion. At some point there are enough oxygen atoms residing in the peroxide compound to support complete combustion of the organics in the molecule (CO₂ + H₂O).[1]

Metal peroxides –

Potassium metal will form peroxides and superoxides (a yellow or orange surface crust) even under mineral oil and may explode violently when handled or cut. There seems to be no chemical test for potassium metal when it comes to peroxide or superoxide formation other than a visual inspection.

III. Acceptable levels of peroxides

According to Kelly and Clark there appears to be no data in the literature for the minimum concentration level of peroxides that is considered safe.[1, 2] It seems that the 100 ppm concentration is widely accepted as the control value based on the practical detection limit of the potassium iodide test method. The potassium iodide test method is an old method for detection of peroxides.[3, 4] It is interesting to note that Kelly mentions that the 100 ppm minimum peroxide value could be “at least an order of magnitude overly conservative in some cases”.[2] The absence of any literature reports detailing safe limits of peroxide concentrations may also have to do with the wide variety of peroxide forming compounds, the mechanisms of their formation and conditions leading to their decomposition. With these complicating factors it is natural that no one has taken on the task to study and report what might be considered dangerous levels of peroxides across a wide spectrum of compounds. Documents on peroxides and Potentially Explosive Compounds (PECs) by the Environmental Health and Safety group at New Mexico State Univ.,[5] and the Chemistry Dept. at Iowa State Univ.[6] mention that the Occupational Safety and Health Administration (OSHA) have no guidelines for acceptable levels for peroxides. A check of the OSHA website confirmed that there is no information to be found on peroxide levels. In general, the maximum level for peroxide concentration in organic compounds, at which most groups deem hazardous, is equal to or greater than 100 ppm.

IV. Styrene – auto polymerization

Occasionally one may encounter seemingly counterintuitive instructions concerning storage of PECs that do not make sense upon hearing. For example, one may hear that some potentially explosive compounds **should not** be stored under inert atmospheres. On the surface this

APPENDIX A. Previous SAND report on peroxide forming chemicals.

V. Determination of peroxide levels

The easiest way to test for peroxide levels is to use peroxide test strips. It has been reported by Kelly that the dip strips (Merck and Aldrich) not only detect hydroperoxides, but also dialkyl peroxides, polyperoxides and cyclic peroxides.[2] These compounds are sometimes not detected by other methods. The detection strips work via a peroxidase enzyme, which transfers oxygen from the peroxide to an organic redox indicator. The indicator will turn blue in the presence of peroxides. For volatile organic compounds Kelly recommends that the test strip be immersed in the chemical for 1 second then the tester should breathe slowly on the test strip for 15 – 30 seconds. This provides a small amount of water from the breath for the reaction to proceed. It is **not recommended** to refrigerate these test strips because moisture will condense on the strips and eventually the water will deactivate them. Therefore it is good practice to keep these test strips in a dry place.

If one does not have peroxide test strips a test for peroxides can be made by preparing a solution of 0.1 g NaI or KI and 1 mL of glacial acetic acid (10% wt/vol). One mL of the NaI/glacial acetic acid solution is added to 1 mL of the material to be tested. The color change may take as long as 10 minutes. A yellow color indicates a low concentration of peroxides (40 – 100 ppm as hydrogen peroxide). A brown color indicates a much higher concentration of peroxide. Blanks must be prepared for comparison. The test solution should be used immediately due to oxidation by air. If glacial acetic acid is not available then HCl or H₂SO₄ may be used at a 20% weight of KI/volume of acid.[1, 2]

VI. Neutralization of peroxides

Situations may exist where one could safely neutralize or dilute peroxides. However, a neutralization procedure would probably have to be reviewed by management and your Safety Officer on a case-by-case basis. **CAUTION – Peroxidized compounds are potentially explosive. Extreme precautions must be taken when handling these compounds. This includes the proper personal protective equipment, blast shields, etc. Do not attempt these neutralizations if you are not qualified.**

Low levels of peroxides (less than 500 to 1000 ppm) can be removed from solvents. If the solvent shows signs of discoloration or there are crystals or layers (a viscous layer), then the neutralization procedure is too hazardous and should not be attempted. Several neutralization methods are given below from the Environmental Health and Safety Website at Berkeley.[9]

Ferrous Salt Method – peroxides can be removed/destroyed from water-soluble solvents by gently shaking with a concentrated solution of ferrous sulfate/acid/water. Be careful, if the solvent contains a high concentration of peroxide this reaction could be exothermic. The ferrous salt solution can be prepared from 60 g of ferrous sulfate (FeSO₄) + 6 mL concentrated sulfuric acid + 110 mL H₂O. Or one can use 100 g of FeSO₄ + 42 mL of concentrated HCl + 85 mL of H₂O.

Activated Alumina Method – for water-insoluble and water-soluble solvents

Peroxides can be removed using activated alumina for both water-insoluble and water-soluble solvents. About 100 g of alumina for 100 mL of solvent can be used. (This method does not work for low molecular weight alcohols.) This procedure removes peroxides from the solvent

APPENDIX A. Previous SAND report on peroxide forming chemicals.

but does not destroy the peroxides. Therefore the alumina must be washed with a dilute acid solution of potassium iodide or ferrous sulfate to destroy the peroxides.

Blue Indicating Molecular Sieves (4-8 mesh, type 4A)[10]

These molecular sieves can be added to peroxidized solvents in the amount of 5 – 10% (weight/volume) of the peroxidized solvent. This process is relatively slow and safe, but could require 1 to 30 days. The peroxide is broken down and the indicator in the sieves is consumed. It is important that the blue indicating molecular sieves are used as it is the Co^{2+} ion that is the key to neutralizing the peroxide.[10] The method is well suited for THF, diethyl ether and di-isopropyl ethers and the neutralization occurs over several days at room temperature. However it is ineffective for dialkyl peroxides.

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APPENDIX B. GUIDELINES FOR PEROXIDIZABLE CHEMICALS¹

Guidelines for Peroxidizable Organic Chemicals

[Corporate Procedure: ESH100.2.IH.4 Evaluate and Control Chemical Hazards](#) contains specific requirements for dating, inspecting, and testing of peroxidizable organic chemicals. Per the Corporate Procedure, testing for peroxide concentration is required at a minimum of every six months for opened containers of peroxidizable organic chemicals. Unopened containers are required to be regularly visibly inspected. Containers of peroxidizable organic chemicals are to be dated upon opening. In addition, there are requirements for updating the corresponding Chemical Information System entry. Refer to Sandia's [ES&H Corporate Procedures](#) for additional requirements involving the use of chemicals at Sandia.

The following guidelines contain valuable information on the management of peroxidizable organic chemicals; including testing procedure and disposal schedules. Use these guidelines in conjunction with the applicable Corporate Procedures and requirements. The accumulation of peroxides in these chemicals may pose a hazard during handling and also result in difficulties in disposing of the material. There are also limitations associated with testing methodologies (e.g., colorimetric test strips). As a result, the Hazardous Waste Management Facility uses 50 parts per million (ppm) peroxide concentration in peroxidizable organic chemical waste as the acceptable limit for pickup and Sandia manages storage at peroxide concentrations less than 30 ppm.

Peroxides can form in solvents, reagents, gases, and solids by the auto-oxidation or peroxidation of a compound with molecular oxygen. The reaction can be initiated by light, heat, introduction of a contaminant, or the loss of an inhibitor. Some chemicals have inhibitors such as BHT (2,6-di-tert-butyl-4-methylphenol) hydroquinone and diphenylamine to slow peroxide formation.

Most organic peroxide crystals formed in peroxide forming chemical liquids are sensitive to heat, shock, or friction, and their accumulation in laboratory reagents has resulted in numerous documented explosions. Organic peroxide vapors and gases increase the pressure within closed containers and can cause the container to rupture causing a fire or damage from the ruptured containers.

Peroxidizable gases pose a potential hazard of rapid polymerization initiated by internally formed peroxides. Although air will not enter a gas cylinder in which gases are stored under pressure, these gases are sometimes transferred from the original cylinder to another in the laboratory, and it is difficult to be sure that there is no residual air in the receiving container.

The peroxide forming compounds recognized of most concern are grouped in the following categories as Lists A through C. Refer to Attachment 1 of this document for the lists of List A-C peroxidizable organic chemicals. There are additional chemicals that may form peroxides, but cannot clearly be placed in these categories. These additional chemicals (List D) may be viewed (with List A-C chemicals) in Table 1 of R.J. Kelly's article titled [Review of Safety Guidelines for Peroxidizable Organic Chemicals](#).

¹Obtained from the Industrial Hygiene Program (04127) webpage under chemical safety.
APPENDIX B. Guidelines for Peroxidizable Chemicals

Hazard List
List A: Severe Peroxide Hazard on Storage with Exposure to Air: May explode even without being concentrated.
List B: Peroxide Hazard on Concentration: Require concentration (such as distillation or evaporation) in order to present a hazard.
List C: Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides

WARNING: DO NOT HANDLE CONTAINERS WITH ANY OF THESE SIGNS

- Crystallization or precipitate in the liquid in the container,
- Crystallization on the lid, cap or exterior of a container,
- Signs of stratification of the liquid in the container,
- The container is deformed (from pressure),
- Other irregularities in the container or contents not consistent with typical handling.

Immediately notify your manager and contact your ES&H Coordinator and [Environmental Compliance Coordinator](#) for instructions on further actions.

Safe Management of Peroxidizable Organic Chemicals

- **Label all containers** when received and update as conditions change (i.e., when opened). Include, at a minimum, Date received, Date opened, and Expiration date.

Peroxide Forming Compound
Received: _____
Opened: _____
Expiration Date: _____

Copy, paste and print using mailing labels

- **Identify peroxide forming chemicals** currently on-site using the *Chemical Regulatory Reports Search Menu, Inventory Report*, listed in the Chemical Inventory System ([CIS](#)). The queries for peroxide forming compounds in the *Regulatory* list are:
 - a. (List A) PEROXIDE - CHEMICALS THAT FORM EXPLOSIVE LEVELS OF PEROXIDES WITHOUT CONCENTRATION
 - b. (List B) PERO_CON - CHEMICALS THAT FORM EXPLOSIVE LEVELS OF PEROXIDES ON CONCENTRATION
 - c. (List C) AUTO POL - CHEMICALS THAT MAY AUTOPOLYMERIZE

APPENDIX B. Guidelines for Peroxidizable Chemicals

This query and the results are only as good as the information contained in CIS. If your inventory is not up to date, your query results will not be either. This query also only looks at chemicals that would have been put in CIS, typically by the JIT vendor; it does not include secondary containers. This query should be considered a tool and not as an all-inclusive approach. Physically look at your inventory to identify any peroxidizable organic chemicals in addition to performing the CIS query. Refer to Attachment 1 of this document for the lists of List A-C peroxidizable organic chemicals.

- **Visually inspect** all peroxide-forming chemical containers (i.e., opened and unopened) before any further evaluation or handling. Containers that exhibit any unusual visual characteristics (see the examples listed under ***Peroxide Test Procedure***) should be assumed to contain dangerous levels of peroxides and should not be disturbed. Notify your manager and contact your ES&H Coordinator and Environmental Compliance Coordinator who will assist in the further evaluation of these suspect containers. Restrict access to the immediate area in which the container is located until it is removed. **If there is any doubt about the safety of handling a chemical container, notify your ES&H Coordinator and Environmental Compliance Coordinator immediately.** Follow applicable emergency procedures for your organization in the event of any emergency situations.
- **Segregate containers of peroxide forming compounds** which have been visually inspected and are not suspect into a separate containment tray to facilitate testing for peroxide formation.
- **Testing & Disposal Schedule:** Perform visual inspection, test and dispose of chemicals following the frequency schedule set in Table 1 using the procedures in the section titled ***Peroxide Testing Procedure***, unless one of the following exceptions is met:
 - Gases in their original pressurized container
 - Solids stored in inert gas or under liquids that eliminate oxygen presence (such as oil or kerosene)
 - Liquids that are always kept in inert atmospheres
 - Containers with specialized closures (such as a septum or Sure/Seal™ cap) when there is an atmosphere of inert gas maintained at all times within the bottle.
 - Liquids or gasses have an inhibitor that prevents peroxide formation and indicates (e.g., color change) the presence of peroxides (such as XPell® www.xplosafe.com).

APPENDIX B. Guidelines for Peroxidizable Chemicals

Table 1: Testing and Disposal Schedule		
Hazard List	Physical State	Testing Frequency and Disposal Schedule
List A: Hazard on Storage with Exposure to Air	Liquid	Dispose of all containers (opened/unopened) at the earliest of manufacturer's expiration date or 24 months of initial receipt. Once opened, test every 3 months.
	Solid	Dispose of all (opened/unopened) containers at manufacturer's expiration date. Testing not applicable.
	Gas	Dispose of all containers at the earliest of manufacturer's expiration date or 36 months of initial receipt. Testing not applicable.
List B: Hazard on Concentration	Liquid	Dispose of all (opened/unopened) containers at the earliest of manufacturer's expiration date or 24 months of initial receipt. Once opened, test every 6 months.
	Solid	Dispose of all containers (opened/unopened) at manufacturer's expiration date. Testing not applicable.
	Gas	Dispose of containers at the earliest of manufacturer's expiration date or 36 months of initial receipt. Testing not applicable.
List C: Hazard of Polymerization by Internally Formed Peroxides	Liquid	Dispose of all (opened/unopened) containers at the earliest of manufacturer's expiration date or 24 months of initial receipt. Once opened, test every 6 months.
	Solid	Dispose of all (opened/unopened) containers at manufacturer's expiration date. Testing not applicable.
	Gas	Dispose of containers at the earliest of manufacturer's expiration date or 36 months of initial receipt. Testing not applicable.

- **Timely Disposal of Materials**

- Dispose of containers prior to their reaching the expiration date listed in the Table 1.
- Label and process waste containers as per the applicable Hazardous Waste Management Corporate Procedures.
- Prior to submitting a Waste Description and Disposal Request ([WDDR](#)) ensure the material has been properly tested for peroxide forming compounds and is below the pickup limit of 50 ppm (i.e., < 30 ppm).

Peroxide Test Procedure

- 1) **Safety Precautions:** Evaluate peroxide-forming chemicals, which have not been managed as specified in Table 1, as follows. Ensure appropriate personal protective equipment (PPE) is worn and chemical manipulations are performed in a laboratory hood. Based on your

APPENDIX B. Guidelines for Peroxidizable Chemicals

organization's procedures, if you are uncertain as to the appropriate PPE and control measures for performing chemical manipulations, contact your [Industrial Hygienist](#).

- 2) **Visual Inspection:** Visually inspect all peroxidizable organic chemicals before proceeding with any further evaluation. Containers that exhibit any unusual visual characteristics, such as the examples listed below, should be assumed to contain dangerous levels of peroxides and should not be disturbed. Only chemicals that pass visual inspection should be evaluated further. Restrict access to the immediate area in which the container is located until it is removed. Inform your manager and notify your ES&H Coordinator and Environmental Compliance Coordinator. They will assist in the further evaluation of the material. If there is any doubt about the safety of handling a chemical container, notify your ES&H Coordinator and Environmental Compliance Coordinator immediately. For any emergency situations, follow applicable emergency procedures for your organization.

Liquid Chemicals

- Crystallization (around the cap or in the liquid)
- Visible discoloration
- Liquid stratification
- Precipitate
- Evaporation of greater than 10%
- Deformity of container (e.g., bulging)

Note: A flashlight or other light source can be used to increase the visibility of the interior of amber bottles. Diethyl ether is commonly sold in steel containers which prevents visual inspection of the liquid. Therefore, diethyl ether containers whose age and use history are unknown should be assumed to contain dangerous levels of peroxides and should not be disturbed.

Solid Chemicals (potassium metal, potassium and sodium amide)

- Discoloration and/or formation of a surface crust (for example, potassium metal forms a yellow or orange superoxide at the surface)

Note: Evaluation of alkali metals and their amides is based on visual criteria only. These substances react strongly with water and oxygen, and standard peroxide tests should not be used.

- 3) **Opening Container:** **Note:** Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.
- Only chemicals that meet the below criteria should be opened and tested for peroxides. Chemicals that do not meet one or more of these criteria should be considered high risk and should not be disturbed. Limit handling and movement; notify your ES&H Coordinator and Environmental Compliance Coordinator.
 - It has been visually inspected and the presence of peroxides is not suspected.
 - The identity of the chemical is known.

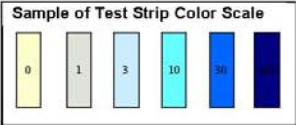
APPENDIX B. Guidelines for Peroxidizable Chemicals

- Evaporation of the chemical is thought to be less than 10% - if this is in question, assume that evaporation has occurred and that high peroxide levels may be present.
- If after opening the container, visual irregularities such as those listed in step 2 are apparent, assume that dangerous levels of peroxides are present. Gently cover the container to minimize evaporation, limit handling and movement, inform your manager and notify your ES&H Coordinator and Environmental Compliance Coordinator as soon as possible. Restrict access to the immediate area in which the container is located until it is removed.

4) Test for Peroxide Concentration in Liquids

Peroxide Test Procedure			
<p style="text-align: center; color: red; font-weight: bold; margin: 0;">WARNING</p> <p style="text-align: center; margin: 5px 0 0 0;">Do not perform testing on any container with the following:</p> <ul style="list-style-type: none"> Indications of peroxide formation Crystals are observed at the cap threads or in the bottle. Crystals of peroxides are EXPLOSIVE when disturbed. Do not touch the container. Prevent it from being handled, notify your manager and contact your ES&H Coordinator and Environmental Compliance Coordinator for instructions on further actions. 			
<ul style="list-style-type: none"> Use safety glasses with side shields, lab coat, and impervious gloves (such as nitrile gloves). Perform test behind a lab hood sash. 			
<p>Test the following types of <u>liquid</u> peroxide forming chemicals:</p> <ul style="list-style-type: none"> Opened containers. Unopened containers once they reach the expiration date or disposal age listed in Table 1. Containers with specialized closures (such as a septum or Sure/Seal™ cap) without provisions to maintain an inert atmosphere within the bottle. Test by removing a small aliquot of peroxide forming compounds using a sampling device such as a syringe, rather than removing the cap. Ion exchange column systems. Secondary containers of peroxide forming compounds that are kept for more than 6 months. 			
<p>Record the test on a label on the container (or indicate a reference to an equivalent written log where this information is kept). Add/replace the following label after each test:</p> <div style="text-align: center; margin: 10px 0;"> <table border="1" style="margin: 0 auto; border-collapse: collapse;"> <tr> <td style="background-color: red; color: yellow; padding: 2px 5px; font-weight: bold;">Peroxide Forming Compound</td> </tr> <tr> <td style="padding: 2px 5px;">List A: Test every 3 months.</td> </tr> <tr> <td style="padding: 2px 5px;">Tested: _____</td> </tr> </table> </div> <p style="text-align: center; margin-top: 10px;">or</p>	Peroxide Forming Compound	List A: Test every 3 months.	Tested: _____
Peroxide Forming Compound			
List A: Test every 3 months.			
Tested: _____			

APPENDIX B. Guidelines for Peroxidizable Chemicals

Peroxide Forming Compound List B, or C: Test every 6 months. Tested: _____
<p>Test results criteria:</p> <ul style="list-style-type: none">• Peroxides in solution <30 ppm PASS the test. Document the test on the bottle label.• Peroxides in solution ≥ 30 but $\leq 1,000$ ppm FAIL the test and need to be treated to remove the peroxides as described in the additional guidance section. If it is not possible to reduce the peroxide concentration, the owner will need to work with the ECC. However, this concentration presents a disposal problem as there is not a current disposal pathway.• Peroxides in solutions > 1,000 ppm FAIL the test. Stop! Secure access to container and contact your ESH Coordinator or Environmental Compliance Coordinator
<p>Perform the test using the following method to detect peroxide compounds in liquids on Lists A, B, and C:</p> <p>Peroxide Test Strips: Indicator strips that turn to an indicative color in the presence of peroxides. Test strips are available from the JIT vendor (e.g., EM Quant® Peroxide Test Strips, 1-100 ppm, SSJ Item #: EMD-10081-1)). Note: these strips must be air-dried until the solvent evaporates and then exposed to moisture for proper operation. Check the expiration date of the test strips. Do not use if expired. Store test strips in a cool (<85F/30C), dry place or refrigerator. Use a test strip only once. In addition, follow any manufacturer specific instructions for use.</p> <p>Aqueous Solutions</p> <ol style="list-style-type: none">1. Remove the test strip from its container/bag and immediately reclose the container.2. Dip the test strip into the solution for 1-2 seconds. Remove the test strip and shake off excess liquid.3. After 30 seconds, compare the test strip to the color scale provided with the test strips. <p>Organic Solutions</p> <ol style="list-style-type: none">1. Remove the test strip from its container/bag and immediately reclose the container.2. Dip the test strip into the solution for 1-2 seconds.3. Remove the test strip. Gently wave the strip in the air until the solvent has evaporated (typically 3-30 seconds).4. Dip the test strip into pure water (e.g., distilled, DI, RO) for 1 second and shake off excess liquid. Water is necessary for the color change to occur.5. After 30 seconds, compare the test strip to the color scale provided with the test strips.
<p>Sample of Test Strip Color Scale</p> 

APPENDIX B. Guidelines for Peroxidizable Chemicals

5) *Additional Guidance*

- Peroxides in solution at concentrations up to about 1,000 ppm do not normally present thermal or shock hazards. Such solutions may be safely treated to remove peroxides.
- Purchase peroxide forming compounds with specialized closures (such as a septum cap) to minimize introduction of air into the container.
- Purchase the smallest quantity of peroxide forming compounds practical for the operations and use on a first-in, first-out basis. Inhibitors are added to some chemicals and the purchase of peroxide formers with added inhibitors is encouraged. However, be aware that these free radical inhibitors will be depleted over time as peroxides are formed. Additionally distillation removes the inhibitor. Distilled peroxide formers and those retained for extended periods should be checked for inhibitor concentration and inhibitor added if below the manufacturer's recommended concentration.
- Store peroxide formers in sealed, air-impermeable containers such as dark amber glass with a tight-fitting cap. Iron inhibits the formation of peroxides in some materials, which is why diethyl ether and some other materials are sold in metal cans. Ground glass stoppered bottles and plastic containers are not advisable, however, plastic squeeze bottles may be used for small quantities of some materials, such as 2-propanol, for immediate use.
- Store polymerizable monomers with a polymerization inhibitor from which the monomers can be separated by distillation just before use.
- Containers of peroxide formers should be stored away from heat and light and protected from physical damage and ignition sources.
- Peroxide forming compounds should not be stored at or lower than the temperature at which the peroxide freezes or precipitates, as this will make these compounds extremely sensitive to shock. Note: refrigeration does not prevent (and may not inhibit) peroxide formation.
- Store peroxide formers, especially those listed in List A, under nitrogen or other inert gas or keep and use them in an inert atmosphere chamber. Note: Some inhibitors actually need small amounts of oxygen to prevent peroxide formation, therefore it is recommended that inhibited chemicals are not stored under an inert atmosphere.
- Avoid the distillation of peroxide formers without first testing for the existence of peroxides. Most explosions occur when a material is distilled to dryness. Leave at least 10-20% in still bottom. Stir such distillations with a mechanical stirrer or an inert gas. Air or an oxygen containing mixture should never be used for this purpose.
- Do not evaporate containers that held peroxide forming compounds to dryness for reuse unless it is known that the chemical was peroxide-free.
- After each use, carefully wipe the container neck, cap and threads with a cloth before resealing.

APPENDIX B. Guidelines for Peroxidizable Chemicals

Examples of specialized closures for containers are shown below:



Septum Cap



Aldrich SureSeal Oxford



Aldrich/Fluka Crown Cap

6) Distillation and Evaporation Precautions

"Prudent Practices in the Laboratory," National Research Council, National Academy Press, Washington, DC, 1995.

- Test all List A or B compounds for peroxides before distillation or evaporation (or treated to positively ensure peroxide destruction). If the material tests positive, it must be disposed of or treated to remove the peroxides. Add a suitable polymerization inhibitor before distilling any List C material.
- Most accidents associated with distillation of peroxidizable compounds have occurred when peroxides have become concentrated in the distillation residue. It is therefore essential to never distill a peroxidizable solvent to a dry residue.
- One solution for compounds showing no more than a trace of peroxide on testing is to discontinue the distillation when a 10 percent heel remains.
- Another solution is to add a high molecular weight inerting solvent, which will not distill, such as mineral oil or a phthalate ester. This solvent will act as a desensitizing diluent for residual peroxides when distillation is complete.
- In addition to safety glasses, use a shield when evaporating or distilling mixtures that may contain peroxides.

7) Removal of Peroxides from Liquids

Removal of Peroxides from Peroxide Forming Liquid Compounds

Only knowledgeable laboratory workers should carry out these procedures. Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principle hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which may also be present in low concentrations. Commonly used peroxide reagents, such as acetyl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and di-t-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.

APPENDIX B. Guidelines for Peroxidizable Chemicals

- **Removal of Peroxides with Alumina**
A 2 x 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 ml of solvent, whether water-soluble or water-insoluble. After passage through the column, test the solvent for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety, it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is properly discarded.
- **Removal of Peroxides with Molecular Sieves**
Reflux 100 ml of the solvent with 5 g of 4- to 8-mesh indicating activated 4A Molecular Sieves for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.
- **Removal of Peroxides with Ferrous Sulfate**
A solution of 6 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 6 ml of concentrated sulfuric acid, and 11 ml of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.

Dialkyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfate, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.
- **Removal of Peroxides with Silicon Oxide/Molybdenum Trioxide (XploSafe Xpell):**
Commercial product that is an antioxidant and indicator. Follow manufacturer's instructions.
- **Destruction of Diacyl Peroxides**
For 0.01 mol of diacyl peroxide, 0.022 mol (10% excess) of sodium or potassium iodide is dissolved in 70 ml of glacial acetic acid and the peroxide is added gradually, stirring at room temperature. The solution is rapidly darkened by the formation of iodine. After a minimum of 30 minutes, the solution may be properly discarded.

Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.
- **Destruction of Dialkyl Peroxides**

One milliliter of 36% (w/v) hydrochloric acid is added to the above acetic acid/potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90° to 100°C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours, before being properly discarded.

APPENDIX B. Guidelines for Peroxidizable Chemicals

Attachment 1: Peroxide-Forming Chemicals

List A. Chemicals that can form explosive levels of peroxides without concentration. (These chemicals should be tested every 3 months instead of 6 months).

Butadiene ^a	Chloroprene ^a
Divinyl acetylene	Isopropyl ether
Potassium amide	Potassium metal
Sodium amide	Tetrafluoroethylene ^a
Vinylidene chloride	

List B. Chemicals that can form explosive levels of peroxides on concentration.

Acetal	Acetaldehyde
Benzyl alcohol	2-Butanol Dioxanes
Chlorofluoroethylene	Cumene (isopropylbenzene)
2-Cyclohexen-1-ol	Cyclohexene
Cyclopentene	Decahydronaphthalene (decalin)
Diacetylene (butadiyne)	Dicyclopentadiene
Diethyl ether	Diethylene glycol dimethyl ether (diglyme)
Ethylene glycol ether acetates (cellosolves)	Furan
4-Heptanol	2-Hexanol
Methyl acetylene	3-Methyl-1-butanol
4-Methyl-2-pentanol	Methyl-isobutyl ketone
2-Pentanol	4-Pentene-1-ol
1-Phenylethanol	2-Phenylethanol
Tetrahydrofuran	Tetrahydronaphthalene
Vinyl ethers	Other secondary alcohols

List C. Chemicals that may autopolymerize due to peroxide formation. The peroxide-forming potential increases for liquids of this group, especially for butadiene, chloroprene and tetrafluoroethylene, such that these materials should be considered as a peroxide hazard.

Butadiene ^b	Chlorobutadiene
Chloroprene ^b	Chlorotrifluoroethylene
Styrene	Tetrafluoroethylene ^b
Vinylidene chloride	Vinyl acetate
Vinyl acetylene	Vinyl chloride
Vinyl pyridine	

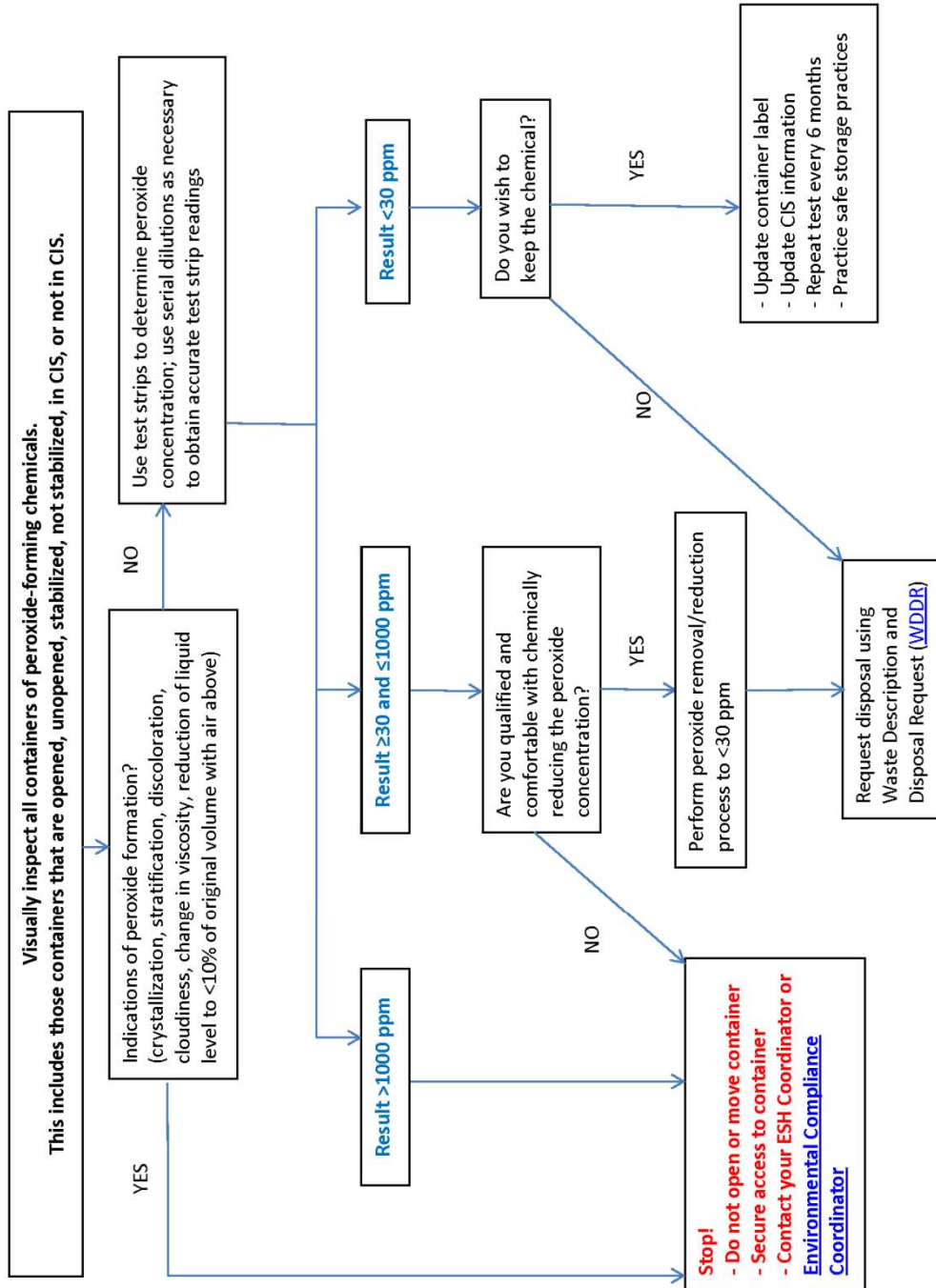
^aWhen stored as a liquid monomer.

^bCan form explosive levels of peroxides when stored as liquid. When stored as gas, peroxide accumulation may cause autopolymerization.

APPENDIX C. SURVEILLANCE OF CHEMICAL INVENTORY FOR PEROXIDE-FORMING CHEMICALS.¹

SURVEILLANCE OF CHEMICAL INVENTORY FOR PEROXIDE-FORMING CHEMICALS

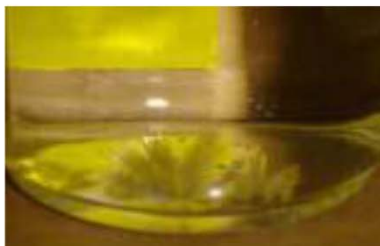
Use the document [Guidelines for Peroxidizable Organic Chemicals](#) for instructions on conducting visual inspection, performing peroxide testing, reducing/removing peroxides from solvents, and safely storing peroxide-forming chemicals. Contact your [Industrial Hygienist](#) for additional support. *Industrial Hygiene has some test strips available for urgent or non-routine use.*



¹Obtained from the Industrial Hygiene Program (04127) webpage under chemical safety.

APPENDIX D. GUIDANCE FOR PEROXIDE-FORMING CHEMICALS¹

Guidance for Peroxide-forming Chemicals



Introduction

Under the appropriate conditions, a number of organic and inorganic chemical compounds used at SNL are capable of reacting with atmospheric oxygen to form peroxide compounds. Many of these peroxides are highly flammable and may explode if exposed to heat, mechanical shock or light.

Peroxide formation in these substances is typically due to auto-oxidation and requires the presence of oxygen. Although auto-oxidation rates vary depending on the molecular structure and physical properties of the peroxide forming compound, as a general rule the rate of peroxide formation is accelerated by exposure to light and heat, and the overall amount of peroxide increases with time.

As purchased, most peroxide-forming compounds contain an inhibitor to prevent peroxide formation and as long as an adequate amount of inhibitor remains in the container peroxide formation is not a problem. (A notable exception to this is HPLC-grade organic solvents that are inhibitor-free.) However, exposure to heat or light during prolonged storage may cause depletion of the inhibitor and lead to peroxide formation.

Common Peroxide-Forming Chemicals

A listing of common peroxide-forming chemicals that may be used at SNL is contained in Attachment A. This attachment contains three lists of chemicals that are grouped according to the hazard mechanism. While these are the most commonly encountered peroxide-forming chemicals, these lists are not all inclusive and do not contain all potential peroxide forming compounds. Consequently, laboratory personnel should consult individual MSDSs or refer to the listed references to identify potential peroxide-forming compounds based upon structural features.

Table 1 lists chemicals that form explosive levels of peroxides during storage and may be an explosion hazard without being concentrated by evaporation or

¹Previously obtained from the Industrial Hygiene Program (04127) webpage under chemical safety (no longer available).

APPENDIX D. Guidance for Peroxide-forming Chemicals

distillation. These compounds are a severe hazard after prolonged storage and all have been involved in fatal accidents.

Table 2 contains chemicals that readily form peroxides through the process of concentration either by evaporation while in storage or by distillation in the lab. As a result, special care and procedures should be used whenever any of these chemicals are distilled in the lab.

Table 3 contains chemicals that are hazardous due to peroxide initiated auto-polymerization. The peroxide-forming potential for compounds in this group increases for chemicals in the liquid state.

Guidelines for Storage and Handling

In addition to the requirements for testing peroxide content in accordance with ESH100.2.IH.4, *Evaluate and Control Chemical Hazards*, the following storage and handling guidelines are recommended for peroxide-forming chemicals.

- Purchase only inhibited chemicals whenever possible.
- Limit quantities to the minimum amount that will be needed within the expiration period of the material.
- Review the Material Safety Data Sheet and/or contact your Division ES&H Team [Industrial Hygienist](#) for the chemical to determine proper handling and storage conditions for the material.
- Label all containers with the date the material was received, the date the container was opened, and the date the material was tested for peroxides.

In general, peroxide forming chemicals should be stored in their original container. These containers should be air-tight and stored away from heat and light. In some cases, the rate of peroxide formation can be minimized by storing the chemical at the lowest possible temperature consistent with the solubility and freezing point of the peroxide. Typically, this means storage in an explosion-proof refrigerator but never in a freezer. Storage of chemicals at temperatures lower than the solubility or freezing point will result in the concentration of hazardous peroxide by freezing or precipitation.

Peroxide-forming chemicals that show visible discoloration, crystallization or liquid stratification are to be treated as potentially explosive. Likewise, older steel containers that have visible rust are also to be treated as potentially explosive. If any of the above conditions are observed, line personnel shall not move or open the container. Contact your division ES&H [environmental compliance coordinator](#) to arrange for an inspection and disposal of the container.

APPENDIX D. Guidance for Peroxide-forming Chemicals

Attachment 1: Peroxide-Forming Chemicals

Table 1. Chemicals that can form explosive levels of peroxides without concentration. (These chemicals should be tested every 3 months instead of 6 months).

Butadiene ^a	Chloroprene ^a
Divinyl acetylene	Isopropyl ether
Potassium amide	Potassium metal
Sodium amide	Tetrafluoroethylene ^a
Vinylidene chloride	

Table 2. Chemicals that can form explosive levels of peroxides on concentration.

Acetal	Acetaldehyde
Benzyl alcohol	2-Butanol Dioxanes
Chlorofluoroethylene	Cumene (isopropylbenzene)
2-Cyclohexen-1-ol	Cyclohexene
Cyclopentene	Decahydronaphthalene (decalin)
Diacetylene (butadiyne)	Dicyclopentadiene
Diethyl ether	Diethylene glycol dimethyl ether (diglyme)
Ethylene glycol ether acetates (cellosolves)	Furan
4-Heptanol	2-Hexanol
Methyl acetylene	3-Methyl-1-butanol
4-Methyl-2-pentanol	Methyl-isobutyl ketone
2-Pentanol	4-Pentene-1-ol
1-Phenylethanol	2-Phenylethanol
Tetrahydrofuran	Tetrahydronaphthalene
Vinyl ethers	Other secondary alcohols

Table 3. Chemicals that may autopolymerize due to peroxide formation. The peroxide-forming potential increases for liquids of this group, especially for butadiene, chloroprene and tetrafluoroethylene, such that these materials should be considered as a peroxide hazard.

Butadiene ^b	Chlorobutadiene
Chloroprene ^b	Chlorotrifluoroethylene
Styrene	Tetrafluoroethylene ^b
Vinylidene chloride	Vinyl acetate
Vinyl acetylene	Vinyl chloride
Vinyl pyridine	

^aWhen stored as a liquid monomer.

APPENDIX D. Guidance for Peroxide-forming Chemicals

^bCan form explosive levels of peroxides when stored as liquid. When stored as gas, peroxide accumulation may cause autopolymerization.

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APPENDIX E. TESTING REQUIREMENTS FOR PEROXIDE-FORMING CHEMICALS¹

Testing Requirements for Peroxide-forming Chemicals

- Date the container when it is first opened and use that date as the initiating date for tracking the testing of peroxide-forming chemicals.
- At the end of 6 months from the container opening date, visually inspect the chemical container prior to handling.
 - If there is evidence of crystallization, cloudiness, or discoloration, peroxidation may have occurred; do not move or open the container.
 - Contact your division ES&H team [environmental compliance coordinator](#) to arrange for disposal.
 - Restrict access to the immediate area in which the container is located until it is removed.
 - If no crystallization, cloudiness, or discoloration is evident, do the following:
 - To ensure continued safe use, test the chemical for peroxide content using a chemical indicator strip (e.g., EM Quant® Peroxide Test Strips, 1-100 ppm, ([SSI](#) Item #: EMD-10081-1)) following the manufacturer's instructions.
 - Chemicals found to contain <30 parts per million (ppm) peroxide, or that can be treated to contain <30 ppm may be retained for an additional 6-month period.
 - Dispose of chemicals with peroxide content at 30 ppm or greater in accordance with the requirements in the following procedures, as applicable:
 - [ESH100.2.ENV.22](#), Manage Hazardous Waste at SNL.
 - [ESH100.2.ENV.15](#), Manage Hazardous Waste at SNL/CA.
 - Document the results of the test in the [Chemical Information System \(CIS\)](#):
 - Select the "Update Container Info" button on the Container Details page for the chemical (the Container Details page is accessed by clicking on any barcode in CIS)
 - Enter the new container expiration date (6 months from current test date)
 - Enter the current test date and results in the container note field
 - Select the "Update" button to save entry
- Re-inspect, test and update the results in CIS for peroxide-forming chemicals every 6 months.
- Regularly inspect containers of unopened, and therefore untested, peroxide-forming chemicals for evidence of crystallization, cloudiness, or discoloration indicating the formation of peroxide. **Note:** Retaining containers of unopened peroxide forming chemicals indefinitely may pose a hazard and result in difficulties in disposing of the chemical. Consider testing and disposal prior to expiration date.

¹Previously obtained from the Industrial Hygiene Program (04127) webpage under chemical safety (no longer available).

APPENDIX F. EXAMPLE CENTER (1800) OP IN PLACE AT SANDIA CONCERNING PPF COMPOUNDS¹

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- When the tax-free alcohol is removed from its original container for experimental use (into a mixture, dispensing container, etc.) it is considered "used" and must be recorded as such.
- The lab owner shall conduct an inventory every six months after receipt to ensure the current (previous) inventory is accurate. Semi-annual inventory results shall be recorded with current inventory data. Any onsite losses shall be reported to the 1800 ESHC
- Records maintained by lab owners shall include:
 - a) Invoices (receipts and shipments)
 - b) Current use inventories
 - c) Semiannual inventory
- Records must be retained for 3 years in the lab Facility Operations Notebook (FON).

9.1.5 Losses that occur on-site must be filed with the BATFE if:

- The loss is > 1% of total location quantity and is more than 10 proof gallons, i.e. spill
- The loss involves theft or unlawful use or removal of any volume

9.1.6 Reporting Losses

- Contact the 1800 ESHC to assist with reporting losses.
- Any onsite losses noted outside of the semi-annual inventory shall also be reported immediately.

9-2 PEROXIDIZABLE CHEMICALS – PROPER STORAGE AND USE

Note: The provisions within this section contain strict requirements regarding the use of peroxideable chemicals due to the high potential for adverse effects from inappropriate use and/or storage thereof.

Note: Further information on shock-sensitive chemicals can be found in the DOE Safety & Health Bulletin (Appendix 11).

9.2.1 Under a variety of conditions, certain organic and inorganic chemical compounds used at SNL are capable of reacting with atmospheric oxygen to form peroxide compounds. Many of these peroxides are highly flammable and may explode if exposed to heat, mechanical shock, friction or light. Serious injury may result if one is exposed to these peroxides should a container rupture.

Peroxidizable chemicals are typically categorized as:

List A: Chemicals that form explosive levels of peroxides without concentration

List B: Chemicals that produce peroxides when stored; there is an increased hazard when concentrated

List C: Chemicals that may autopolymerize due to peroxide formation

The chemicals usually listed by various organizations and universities. List A is fairly consistent among these groups. List B shows more variation and List C even more. But, the bottom line is that care needs to be used with these chemicals.

The CIS Regulatory Lists below show which report you can pull for your lab space. Appendix 8 lists the chemical for these categories that are currently looked for in CIS.

Report names in CIS are:

PEROXIDE – CHEMICALS THAT FORM EXPLOSIVE LEVELS OF PEROXIDES WITHOUT CONCENTRATION – A List

PERO_CON – CHEMICALS THAT FORM EXPLOSIVE LEVELS OF PEROXIDES ON CONCENTRATION – B List

AUTO_POL – CHEMICALS THAT MAY AUTOPOLYMERIZE DUE TO PEROXIDE FORMATION – C List

9.2.3 While these are the most commonly encountered peroxide-forming chemicals, these lists are not all inclusive and do not contain all potential peroxide-forming compounds. Consequently, chemical users shall always consult individual MSDS documents to ensure they are aware of all chemical hazards.

9.2.4 Peroxide-forming chemicals have different inherent potentials for forming peroxides, as designated by chemical groups, and therefore some are potentially more hazardous than others. Users can contact the 1800 CST IH for guidance regarding the relative potential for peroxide formation.

¹Obtained from 1800 SharePoint.

APPENDIX F. Example center (1800) OP in place at Sandia concerning PPF compounds.

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9.2.5 Chemical owners and users shall be responsible for the safe use and storage of any chemical and especially peroxide-forming chemicals.

9.2.6 Chemical owners and users shall implement one or more of the following controls to minimize the formation of peroxides and to affect proper handling and storage:

- Purchase chemicals that contain an oxidation inhibitor whenever possible.
- Limit quantities to the minimum amount that will be needed within the expiration period of the chemical. **A better price for a larger quantity should never be considered.**
- Review the MSDS for the chemical to determine proper handling and storage conditions for the material.
- Store in appropriate location in the original container whenever possible and ensure the lid is always airtight.
- Store away from heat and light.
- Label all containers with the following:
 - a) the date the material was received
 - b) the shelf life of the chemical and the expiration date (if not already listed on the manufacturer's label)
 - c) the date the container was opened.
- If tested for peroxide buildup, include such information on the label.
- Chemical owners/users shall be responsible for conducting the testing of peroxide levels.
- For those chemicals that form peroxides on concentration, mark and date the liquid level on the bottle, if possible, after each use. This will allow personnel to note whether there has been leakage or evaporation from the bottle during storage. Leakage or evaporation may lead to build-up of peroxide forming compounds.
- Use or dispose of the containers by the expiration date. If an expressed interest exists to retain the chemical beyond the expiration date, a measurement of peroxide levels using an oxidizer test strip shall be taken and documented. This information should be kept in the laboratory FON.
- Containers of peroxide chemicals shall be retested at frequencies sufficient to assure that the peroxide levels will not exceed 30 ppm during continued storage. Peroxide levels of 30 ppm or greater require the chemical to be disposed of immediately.

9.2.7 Safe retention dates for chemicals are noted in Appendix (8).

9.2.8 No container may be kept beyond 2 years of purchase even with monitoring of peroxide levels unless a *Justification of Retention* form (Attachment A) is completed and approved.

9.2.9 Possibly Out-of-date Material

- Chemical owners and users shall treat containers of peroxidizable chemicals that meet one or more of the criteria listed below as potentially explosive:
 - a) Two years beyond purchase date.
 - b) Of unknown history.
 - c) Show visible discoloration, crystallization or liquid stratification.
 - d) Show visible rust, (e.g., older steel containers).
- If any of the above conditions exist, lab owners/chemical users shall:
 - a) Not move or open any container that meets one or more of the above conditions.
 - b) Take appropriate actions to isolate or secure access to such containers.
 - c) Immediately contact the:
 - 1800 ESHC
 - 1800 CST ECC (to arrange for an inspection and disposal of the container).

9.3 OTHER THAN AMBIENT PRESSURE GLASSWARE – CONSTRUCTION AND SAFE OPERATIONS

9.3.1 Glass is the material of choice for a variety of vacuum and pressure operations in any chemical laboratory because it is typically chemically inert and transparent – allowing viewing of chemical actions. While glass generally performs well, its reliability cannot be taken for granted. Failure, though rare, is unpredictable and could result in:

- an explosion (if contained pressure is greater than outside pressure)
- an implosion (if outside pressure is greater than contained pressure)

APPENDIX G. WATERWORKS™ MANUAL DESCRIPTION.¹

Peroxide (H₂O₂)



ITS' Peroxide strips develop color through enzymatic (HRP) reaction with H₂O₂ to form a blue dye (indicator TMB). Typical concentrations of ions found in tap water do not interfere. The presence of strong oxidizing agents, however, can interfere. Acceptable pH levels are from 2 to 9 as long as the solution is not buffered. Strong alkali or acidic samples should be adjusted to pH 5 to 7. For hydroperoxide determination in organic solvents, moisten the test pad (480014) with the solvent, allow to evaporate and dry, then moisten again with a drop of distilled water. Any blue indicates the presence of hydroperoxide. Extensively used in the food and dairy industries, our peroxide (480014 and 481015) strips confirm that residual peroxide sanitizer has been fully purged from containers, equipment, and filling lines before use.

Test uses HRP enzyme with TMB which forms a blue color in the presence of Peroxide.

Peroxide is one of the most powerful oxidizers known – stronger than chlorine, chlorine dioxide, and potassium permanganate.

Peroxide can both inhibit and encourage microbial growth. Similarly, it can treat both easy-to-oxidize pollutants (iron and sulfides) and difficult to-oxidize pollutants (solvents, gasolines and pesticides).

By simply adjusting the conditions of the reaction (e.g., pH, temperature, dose, and/or reaction time), Peroxide can often be made to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant.

Peroxide has none of the problems of gaseous releases or chemical residues that are associated with other chemical oxidants. Also, Peroxide is totally miscible with water. Therefore, concentration dictates its safety.

WaterWorks™ Low Range Peroxide Check
For further accuracy, hold the test strip in half so that the white handle exposes the underside of the aperture window.

TEST PROCEDURE:
 DIRECTIONS: Dip one test strip into a 250 ml (8oz) water sample with constant, gentle back-and-forth motion for 5 seconds. Remove the strip, shake once, briskly, to remove excess water and wait 15 seconds. Then, view through the aperture to match with the closest color. Complete color match within the next 30 seconds. Read ppm of Peroxide as Hydrogen Peroxide (H₂O₂).

sample color chart

PPM (mg/L)	0.05	0.3	0.5	1.0	2.0	4.0

Cat. No.	Detection Levels:	Test Methodology:	Test Time:	No. of Tests:	Price:
480014	0, 0.5, 2, 5, 10, 25, 50, 100 ppm (mg/l)	Colorimetric	30 Seconds	Bottle of 50	\$12.99
481015	0, 0.05, 0.3, 0.5, 1, 2, 4 ppm (mg/l)	Colorimetric	20 Seconds	Bottle of 50	\$18.99
481116	0, 200, 400, 800, 1600, 2500, 5000, 10000, 30000 ppm (mg/l)	Colorimetric	25 Seconds	30 Packets	\$15.99

Order online at www.sensafe.com

Call 1-800-861-9742

Fax 1-803-329-9743

¹Obtained from a distributor of WaterWorks™ peroxide testing strips.

APPENDIX H. MQUANT™ 1-100 PPM TEST STRIP INSTRUCTIONS.¹

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February 2013

1.10011.0001
1.10011.0002
1.10081.0001

MQuant™ Peroxide Test



1. Method

Peroxidase transfers peroxide oxygen to an organic redox indicator. This produces a blue oxidation product. The peroxide concentration is measured **semi-quantitatively** by visual comparison of the reaction zone of the test strip with the fields of a color scale.

2. Measuring range and number of determinations

Cat. No.	Measuring range / color-scale graduation mg/l H ₂ O ₂	Number of determinations
1.10011.0002	0.5 - 2 - 5 - 10 - 25	25
1.10011.0001		100
1.10081.0001	1 - 3 - 10 - 30 - 100	100

3. Applications

This test measures inorganic peroxides in aqueous solutions and organic solvents. Polymeric peroxides are not at all or only incompletely measured.

Sample material:

Simple ethers
UHT milk
Pickling and copper-stripping baths
Bleaching and oxidizing agents (paper and textile industries)
Disinfectant and rinsing solutions (e.g. food technology, laundries)
Swimming-pool water

4. Influence of foreign substances

This was checked in solutions with hydrogen peroxide concentrations from the middle of the respective measuring range and with 0 mg/l H₂O₂. The determination is not yet interfered with up to the concentrations of foreign substances given in the table.

Concentrations of foreign substances in mg/l			
CrO ₄ ²⁻	10	IO ₃ ⁻	40
[Fe(CN) ₆] ⁴⁻	10	MnO ₄ ⁻	2
[Fe(CN) ₆] ³⁻	10	S ₂ O ₈ ²⁻	20
Hg ⁺	250	VO ₃ ⁻	5

5. Reagents and auxiliaries

The test strips are stable up to the date stated on the pack when stored closed at +2 to +8 °C.

Package contents:

Tube containing 25 test strips
(Cat. No. 1.10011.0002)
or
containing 100 test strips
(Cat. Nos. 1.10011.0001 and 1.10081.0001)

Other reagents:

MColorHast™ Universal indicator strips pH 0 - 14, Cat. No. 109535
Sodium acetate anhydrous GR for analysis, Cat. No. 106268
Hydrochloric acid 1 mol/l TitriPUR®, Cat. No. 109057
Diethyl ether for analysis EMSURE®, Cat. No. 100921
Hydrogen peroxide 30 % H₂O₂(Perhydrol®) GR for analysis, Cat. No. 107209

6. Preparation

- Samples containing more than 25 mg/l H₂O₂ (Cat. Nos. 110011) or 100 mg/l H₂O₂ (Cat. No. 110081) must be diluted with distilled water or peroxide-free ether.
- The pH of the aqueous sample must be within the range 2 - 12. If necessary, buffer the sample with sodium acetate or, respectively, adjust the pH with hydrochloric acid.

7. Procedure

Protect the reaction zones from light (also during the reaction time)!

Determination in aqueous solutions:

Immerse the reaction zone of the test strip in the pre-treated sample (15 - 30 °C) for 1 sec.
Allow excess liquid to run off via the long edge of the strip onto an absorbent paper towel and after 15 sec (Cat. No. 110011) or after 5 sec (Cat. No. 110081) determine with which color field on the label the color of the reaction zone coincides most exactly.
Read off the corresponding result in mg/l H₂O₂.

Determination in organic solvents (readily volatile ethers):

Immerse the reaction zone of the test strip in the pre-treated sample (15 - 30 °C) for 1 sec.
After the solvent has evaporated (gently fan the strip back and forth for 3 - 30 sec), immerse the reaction zone in distilled water for 1 sec and allow excess liquid to run off via the long edge of the strip onto an absorbent paper towel.
After 15 sec (Cat. No. 110011) or after 5 sec (Cat. No. 110081) determine with which color field on the label the color of the reaction zone coincides most exactly.
Read off the corresponding result in mg/l H₂O₂.

Notes on the measurement:

- Every blue colouration within 3 min can be interpreted as a positive result.
- If the color of the reaction zone is equal to or more intense than the darkest color on the scale or if another color emerges, repeat the measurement using fresh samples diluted with distilled water or, respectively, peroxide-free ether until a value of less than 25 mg/l H₂O₂ (Cat. No. 110011) or 100 mg/l H₂O₂ (Cat. No. 110081) is obtained.
In the case of Cat. No. 110081 the reaction zone indicates values within the measuring range also for H₂O₂ contents from 5000 mg/l (0.5 %) up.
In such cases it is advisable to conduct a plausibility check of the measurement results by diluting the sample (e.g. 1:10, 1:100).

Concerning the result of the analysis, the dilution (see also section 6) must be taken into account:

Result of analysis = measurement value x dilution factor

8. Method control

To check test strips and handling:
Make up 5.0 ml of Perhydrol® (H₂O₂ 30 % ± 333.000 mg/l H₂O₂) to 500 ml with distilled water and mix. Take 1.5 ml of this solution, make up to 500 ml with distilled water, and mix. Subsequently analyze immediately (solution is not stable) as described in section 7. The content of H₂O₂ determined should be 10 mg/l.

Additional notes see under www.qa-test-kits.com.

9. Note

Reclose the tube containing the test strips immediately after use.

Merck KGaA, 64271 Darmstadt, Germany,
Tel. +49(0)6151 72-2440
www.analytical-test-kits.com

EMD Millipore Corporation, 290 Concord Road,
Billerica, MA 01821, USA, Tel. +1-978-715-1335



¹Obtained from an MQuant™ Technical Services Specialist.

APPENDIX I. MQuant™ 100-1000 PPM TEST STRIP INSTRUCTIONS.¹

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February 2013

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MQuant™ Peroxide Test



1. Method

Peroxidase transfers peroxide oxygen to an organic redox indicator. This produces a yellow-brown oxidation product. The peroxide concentration is measured **semiquantitatively** by visual comparison of the reaction zone of the test strip with the fields of a color scale.

Each strip also features a second reaction zone (**alert zone**). This zone changes color in the presence of high peroxide concentrations (from approx. 2000 mg/l H₂O₂ on) and of interfering concentrations of peracetic acid.

2. Measuring range and number of determinations

Measuring range / color-scale graduation	Number of determinations
100 - 200 - 400 - 600 - 800 - 1000 mg/l H ₂ O ₂	100

3. Applications

Determination of inorganic peroxides in aqueous solutions

Sample material:
Disinfectant solutions

4. Influence of foreign substances

This was checked in solutions with 400 and 0 mg/l H₂O₂. The determination is not yet interfered with up to the concentrations of foreign substances given in the table. Interfering concentrations of peracetic acid are indicated by the alert zone.

Concentrations of foreign substances in mg/l or ‰		
Ascorbate	100	Free chlorine (hypochlorite)
Ca ²⁺	500	Combined chlorine (chloramine T)
Fe ²⁺	5	Formaldehyde
Fe ³⁺	5	Total hardness
NO ₃ ⁻	500	
SO ₄ ²⁻	100	

5. Reagents and auxiliaries

The test strips are stable up to the date stated on the pack when stored closed at +2 to +8 °C.

Package contents:
Tube containing 100 test strips

Other reagents:
MColorpHast™ Universal indicator strips pH 0 - 14, Cat. No. 109535
Sodium hydroxide solution 1 mol/l TitriPUR®, Cat. No. 109137
Sulfuric acid 0.5 mol/l TitriPUR®, Cat. No. 109072
Hydrogen peroxide 30 % H₂O₂ (Perhydrol®) GR for analysis, Cat. No. 107209

6. Preparation

- Samples containing more than 1000 mg/l H₂O₂ must be diluted with distilled water.
- The pH must be within the range 2 - 7. Adjust, if necessary, with sodium hydroxide solution or sulfuric acid.

7. Procedure

Protect the reaction zones from light (also during the reaction time)!

Immerse **both reaction zones** of the test strip in the pre-treated sample (15 - 25 °C) for **1 sec.**
Shake off excess liquid from the strip and **after 30 sec** determine with which color field on the label the color of the H₂O₂ reaction zone coincides most exactly. **The color of the alert zone must not change to blue during this time!**
Read off the corresponding result in mg/l H₂O₂.

Notes on the measurement:

- The color of the reaction zone may continue to change after the specified reaction time has elapsed. This must not be considered in the measurement.
- In the event that the alert zone changes color, the reaction zone may indicate false-low peroxide concentrations!
- If the color of the reaction zone is equal to or more intense than the darkest color on the scale, repeat the measurement using **fresh**, diluted samples until a value of less than 1000 mg/l H₂O₂ is obtained.

Concerning the result of the analysis, the dilution (see also section 6) must be taken into account.

Result of analysis = measurement value x dilution factor

8. Method control

To check test strips and handling:
Make up 1.8 ml of Perhydrol® (H₂O₂ 30 % ± 333 000 mg/l H₂O₂) to 1 l with distilled water, mix, and analyze **immediately** (solution is not stable) as described in section 7. The content of H₂O₂ determined should be 600 mg/l.
Additional notes see under www.qa-test-kits.com.

9. Note

Reclose the tube containing the test strips immediately after use.

Merck KGaA, 64271 Darmstadt, Germany,
Tel. +49(0)6151 72-2440
www.analytical-test-kits.com

EMD Millipore Corporation, 290 Concord Road,
Billerica, MA 01821, USA, Tel. +1-978-715-1935



¹Obtained from an MQuant™ Technical Services Specialist.

Literature

Product Literature / Application Notes

10011 EM Quant[®] Peroxide Test

Test strips and reagent for the detection and semi-quantitative determination of peroxides

General

The Peroxide Test detects inorganic and organic compounds containing a peroxide or a hydroperoxide group. It is well suited to the routine checking of simple ethers such as diethyl ether (ethyl ether), tetrahydrofuran and dioxan. The polymeric peroxides sometimes occurring in simple ethers are only detected with reduced sensitivity, if at all. This being so, it is advisable to perform a trial determination in the laboratory to verify that the Peroxide Test strip gives satisfactory results.

As well as for checking ethers, this product can be used to test UHT milk for residual peroxide, to measure perborates in washing powders, to check electrolytic etching and copper stripping baths, to test peroxides used as bleaches or oxidants in paper manufacture and the textile industry, and to determine peroxides in swimming pool water.

Peroxide is an excellent bactericide, fungicide and virucide which does not produce harmful decomposition products. These properties and also the fact that it is a very versatile disinfectant (used sometimes in combination with peracetic acid), make peroxide suitable for use in the food industry. Here, the Peroxide Test can be used **not only** to monitor disinfectant concentrations but also to test for residues on equipment after cleaning and rinsing.

Principle of the Method

Peroxidase (POD) transfers oxygen from peroxide to an organic redox indicator, which is converted to a blue oxidation product.

When organic solvents are tested, the moisture required for the reaction to occur is provided by breathing on the reaction zone several times or by immersing in distilled water.

Graduation

0 - 0.5 - 2 - 5 - 10 - 25 mg/l (ppm) H₂O₂

Directions

Aqueous solutions:

http://www.emscience.com/Literature/311025_Environmental^Testing_EM^QUANT^Test... 11/1/2002

¹Obtained from an MQuant[™] Technical Services Specialist.

APPENDIX J. EM Quant[®] Technical notes.

1. Remove a test strip and close the container **immediately**.
2. Immerse the test strip in the sample solution for 1 second, so that the reaction zone is thoroughly moistened.
3. Remove the test strip, gently shake off excess liquid, wait 15 seconds and compare the reaction zone with the color scale.

Notes

The sample solution should be between pH 2 and 12.

Strongly acidic solutions (pH <2) must be buffered with sodium acetate; strongly alkaline solutions (pH >7) with citric acid.

The appearance of a blue color within 3 minutes can still be interpreted as a positive reaction.

If the zone turns deep blue, green or brown, the peroxide concentration is too high, in which case the sample must be diluted.

Use in Dairies

In dairies checks must be made on the diethyl ether peroxide concentration of the extraction ether used for fat determinations and on hydrogen peroxide levels in salt baths, peroxide-containing disinfectants and other liquids. Peroxide concentrations must be monitored in the preparation of sterilized (UHT) milk. The packaging material used for flexible containers is disinfected by passing it through a hydrogen peroxide bath. At the point of sale, however, the milk must not contain any peroxide.

The Peroxide Test can also be used to distinguish between fresh milk and milk which has turned slightly sour. Sour milk contains pyruvate, which reacts with hydrogen peroxide. The amount of hydrogen peroxide used up in the reaction forms the basis of a simple test:

Add a known quantity of H₂O₂ (1 to 10 drops, 0.3%) to a known volume of milk (e.g. 10 ml) and shake well. After a defined reaction time (e.g. 3 minutes) briefly immerse a Peroxide Test strip in the mixture and then remove. Fresh milk produces a blue color on the reaction zone, while sour milk leaves it white because all of the H₂O₂ is consumed by the pyruvate. Fresh milk typically produces a slight blue coloration following addition of 2 drops of 0.3% H₂O₂, while 7 drops are required if the milk is sour.

We have deliberately left the procedure rather vague and leave it to individual milk testing stations to select the amount of milk taken, the number of drops of reagent to be added and the reaction time.

Organic Solvents

Volatile Ethers

http://www.emscience.com/Literature/311025_Environmental^Testing_EM^QUANT^Test... 11/1/2002

APPENDIX J. EM Quant[®] Technical notes.

EM Quant[®] Technical Notes

Page 5 of 6

1. Immerse a test strip for approximately 1 second in the solvent being tested and allow to evaporate.
2. Breathe on the reaction zone 4 times for 3-5 seconds each time. Alternatively, immerse briefly in distilled water.
3. Compare the reaction zone with the color scale.

Low Volatility Ethers

A. Immiscible with water.

1. Mix a sample of the ether to be tested with 3 times its volume of peroxide-free ether or petroleum benzine (boiling range 40-60°C).
2. Test as described under "Volatile ethers."
3. Record the value indicated on the scale and multiply by 4.

B. Miscible with water

1. Mix a sample of the ether to be tested with 3 times its volume of distilled water.
2. Immerse a test strip for approximately 1 second.
3. Wait 2 minutes and compare with the color scale.

Convert the results as under "Conversion."

Conversion

Allowing for dilution, 3 mg/l on the color scale is equivalent to:

90 mg/l tetrahydrofuran peroxide or 30 mg/l peroxide calculated as H₂O₂

150 mg/l dioxan peroxide or 45 mg/l peroxide calculated as H₂O₂.

Notes

If a dark blue to brown or a green to brown color is produced, the peroxide concentration is too high for the color scale. In this case dilute with water, peroxide-free ether or petroleum benzine (boiling range 40-60°C) as appropriate, and test as directed.

Inorganic peroxides are determined in aqueous solution at pH 2-12. Measure the pH with non-bleeding universal indicator strips (pH 0-14) Item #9590-3. If necessary, adjust the pH of the solution with citric acid or 1 mol/l sulfuric acid, or with sodium citrate or sodium acetate as appropriate.

For ethylene glycol monoethyl ether containing 4-50 mg/l ethylene glycol monoethyl ether peroxide, proceed as follows:

Mix a sample of the solvent with an equal volume of fully demineralized water. Briefly

http://www.emscience.com/Literature/311025_Environmental^Testing_EM^QUANT^Test... 11/1/2002

immerse a test strip in the aqueous phase, wait 15 seconds and compare the reaction zone with the color scale. Multiply the value obtained by 4 to give the peroxide content in mg H₂O₂ per liter of ethylene glycol monoethyl ether.

Unlike with the conventional methods used to determine ether peroxides, the Peroxide Test strips allow peroxides to be concentrated by repeatedly immersing and breathing on the reaction zone. Immersing a strip once and breathing on it three times enables as little as 5 mg/l diethyl ether peroxide to be detected by matching against the lowest value on the scale, and as little as 2 mg/l to be estimated. When this procedure is repeated 5 times, as little as 0.5 mg/l of diethyl ether peroxide (~2.5 x 10⁻⁵% hydrogen peroxide) can still be clearly detected. Not only is this method of detection just as sensitive as the conventional reaction of ether peroxide with potassium iodide in solution (DAB 6 determination), it also gives a reading of the same ether peroxide concentrations in a matter of minutes as opposed to an hour. The conventional potassium iodide/starch paper (which just about enables 20 mg/l ether peroxide to be detected) is far less sensitive than the Peroxide Test strips.

Use in Organic Solvents

It is generally recognized that ether peroxides are dangerous. However, the danger is often underestimated when ethers are being distilled, resulting in explosions which could really be avoided. Explosions can also occur when containers of peroxide-containing liquids are jolted or the peroxides ignite as a result of friction upon opening. This type of risk is inherent not only in ethers such as diethyl ether, diisopropyl ether, dioxan and tetrahydrofuran, but also in other liquids which show a tendency to form peroxides. These include unsaturated hydrocarbons, aldehydes, ketones and tetralin. In order to prevent accidents, these liquids must be tested for peroxides at regular intervals and again prior to their use. The Peroxide Test is extremely useful for performing rapid, reliable, semi-quantitative checks for the presence of hydroperoxides and ether peroxides. It is therefore ideal as a routine test for simple ethers such as diethyl ether, tetrahydrofuran and dioxan. Polymeric peroxides, which occasionally form in diethyl ether, are not detected. The following peroxides either do not react or do so with considerably reduced sensitivity: tert-butyl perbenzoate, dicumyl peroxide, di-tert-butyl peroxide and 1,3-cyclooctadiene. In these cases preliminary testing is recommended, since varying the test conditions sometimes enables a reproducible result to be obtained, or at least a qualitative indication that peroxides are present. Samples should be analyzed simultaneously in the laboratory to verify the suitability of the test strips for the particular test envisaged. What's more, special attention must be given to the expiration date for the test. Control determinations may be needed on ethers of known peroxide content.

Polymeric peroxides produce a yellow or orange color with titanium sulfate in 50% sulfuric acid.

Notes on the Handling of Diethyl Ether

Ether must never be distilled to dryness. When the volume of ether is large, even an initial peroxide content so low as to remain undetected may build up to a dangerous level.

APPENDIX J. EM Quant[®] Technical notes.

It is advisable to test ethers regularly and whenever they are about to be used.

Numerous methods of destroying peroxides have been proposed. All of these offer only a partial solution, however. For example, in water-immiscible solvents, hydroperoxides may be removed while polymeric peroxides are not.

A method of removing peroxide:

Shake before use with a freshly prepared solution of iron (II) sulfate (for each liter of ether, use 5 g iron (II) sulfate dissolved in 20 ml water). Repeat until no more peroxide is detected with strip.

Air Testing

A moistened Peroxide Test strip can be used to measure peroxide levels in air. Briefly dip the test strip in water, shake off surplus liquid and expose to the air for 10 minutes. Then match the color.

Matched color Value	Concentration of gaseous H ₂ O ₂
1 ppm	0.7 mg/m ³
3 ppm	5 mg/m ³
10 ppm	25 mg/m ³
30 ppm	50 mg/m ³
100 ppm	500 mg/m ³

Influence of Cations and Anions

A green to blue coloration of the reaction zone at pH 5-6 is caused by more than 5 mg/l Au³⁺, 5 mg/l Ce⁴⁺, 250 mg/l Hg⁺, 10 mg/l CrO₂⁻⁴, 10 mg/l [Fe(CN)₆]³⁻, 40 mg/l O₄, 2 mg/l MnO₄, 20 mg/l S₂O₂⁻⁸ or 5 mg/l VO⁻³ as well as by Br₂ and Cl₂.

Elimination of Interfering Ions

The oxidizing anions listed above can be removed with Amberlite[®] IRA-400 ion exchanger. Fill a glass column (diameter 5-10 mm) with approximately 1 g ion exchanger and allow the test solution, adjusted to pH 5-6 with 1 mol/l hydrochloric acid or 1 mol/l sodium hydroxide solution to run through the column slowly (1 drop/second). Test the eluate for peroxide. At below pH 1.5, Au³⁺ is separated as AuCl⁻⁴ by the ion exchanger. Hg⁺ is precipitated by adding sodium chloride. Ce⁴⁺ is masked by adding a small spatula tip of potassium fluoride to about 5 ml of the test solution.

Standard (1000 mg/l)

http://www.emscience.com/Literature/311025_Environmental^Testing_EM^QUANT^Test... 11/1/2002

APPENDIX J. EM Quant[®] Technical notes.

10011 EM Quant[®] Peroxide Test

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Add approximately 0.33 ml of 30% Perohydrol to approximately 100 ml of distilled water and find the exact concentration by titrimetry. Dilute to the required strength.

Package Size

10011 EM Quant[®] Pack of Peroxide Test 100 test strips

http://www.emscience.com/Literature/311025_Environmental^Testing_EM^QUANT^Test... 11/1/2002

APPENDIX K. ORGANIC PEROXIDE TEST STRIP COMPARISON EXERCISE.¹

ORGANIC PEROXIDE TEST STRIP COMPARISON EXERCISE

4/1/2013- AML

Purpose- The purpose of this exercise was to compare the two major brands of peroxide test strips, (EM QUANT, and WATERWORKS), currently in use at SNL and its off-site locations to evaluate their performance using peroxide solutions of known concentrations. The two major goals of the exercise were to examine the accuracy of the strips, and to verify and validate the reading time periods for the two strips. Additional insights that we were hoping to attain were to validate a higher range strip in order to help provide guidance when high readings (>100 PPM) are found in routine field testing of peroxide forming chemicals are found, and we evaluated the strips as to the effects of excess light during testing.

Procedure- The two types of test strips- EM QUANT- range 0-100 PPM (expiration date 5/13), and WATERWORKS- range 0-100 PPM (expiration date 8/13) were dipped in 10, 50, 100 PPM solutions of a freshly prepared hydrogen peroxide solution and color readings/observations were taken by four people present at 5 seconds, 30 seconds, 1 minute, and three minutes to note changes in the coloration during this timeframe, as well as general accuracy of the strips to the corresponding PPM solutions. The tests were also made with, and in the absence of direct light, to test the effects of light on color development in the strips. Observations and trends were recorded throughout the process. This procedure was adapted from the manufacturers recommended verification procedure found in the product insert for the EM QUANT strips.

Findings and Observations-

General summary of Observations/Measurements-

For the Waterworks 0- 100 PPM strips, all concentrations (10, 50, 100 PPM), The strip color corresponding to the known concentration of the peroxide solution was fully developed between the 5 second time interval and the 1 minute interval, and remained stable well past the 3 minute reading. The stabilized color on the strip was an accurate representation of the known concentration, i.e. 10 PPM solution corresponded well to the 10 PPM color on the color chart on the container, and similarly for the other peroxide concentrations.

For the EM Quant 0-100 PPM strips, all concentrations (10, 50, 100 PPM), The strip colors corresponding to the known concentrations of the peroxide solutions were continuously developing during the time intervals between 5 seconds and 3 minutes, and was not as accurate in representing the actual concentrations of the standards as the Waterworks strips testing the same solutions. At the 5 second observation, the color was quickly developing and continued to develop. The consensus on the reading of the strip dipped in the 10 PPM solution was that it was comparable to about 15 PPM on the color chart. Similarly, the 50 PPM and 100 PPM solutions read around 65 and > 100 PPM respectively during the first minute of the time interval. It was difficult to pinpoint an actual reading time with this strip because the color change continued to develop throughout the entire 5 second to three minute time interval, and it read high throughout the period.

¹Obtained from the Hazardous Waste Handling Facility.

APPENDIX K. Organic peroxide test strip comparison exercise.

that these tests are qualitative only, and sometimes subject to interferences, and that phenotypic or physical clues such as, crystal formation, discoloration, striations of the chemical are valuable information as well.

APPENDIX L. HAZARDOUS WASTE HANDLING FACILITY PEROXIDE FORMING
CHEMICALS EVALUATION FORM.¹



Sandia National Laboratories

RF 2042-PFC (0609, Rev. 0)

**Hazardous Waste Management Facility (HWMF) Organic
Peroxide and Peroxide Forming Chemicals Evaluation Form**

A. General Information

Point of Contact (POC): Name: _____ Phone: _____

Location: Building # _____ Room # _____

Associated WDDR: _____

Is safety equipment and LEV required by Section D, available in the lab?

Comment: _____

B. Process Knowledge:

1) Chemical Name: _____

2) CIS #: _____

3) Date of Purchase: _____ Indicated on bottle? Yes No

4) Date first opened: _____ Indicated on bottle? Yes No

5) Expiration date: _____ Indicated on bottle? Yes No

6) Stabilized: Yes No If Yes, with what? _____

Is the Stabilizer name and concentration on the bottle? Yes No

C. Visual Investigation:

7) Housekeeping in the lab acceptable? Yes No
Proper entrance and exit spacing: Yes No
Proper segregation of chemicals: Yes No
Fume hood free of incompatibles: Yes No

8) Is the Compound in its original bottle? Yes No
If not, is the current labeling clear, accurate and complete? Yes No

9) Other Organic Peroxides or PFCs in the laboratory? Yes No
- Any failed peroxide tests? Yes No
- Any show evidence of crystallization? Yes No
- Relative age of those compounds: Same Age Newer Older

10) Evidence of crystallization on the bottle or around the cap? Yes No

If Yes, Stop Immediately. Go to Step 6(B), Section G.

11) Indication of crystal or peroxide formation in the compound (Use Flashlight)?
- Stratification of the liquid Yes No
- Precipitate in the liquid Yes No
- Crystals in suspension Yes No
- Discoloration of the liquid Yes No

If Yes to any of the above, Stop immediately. Go to Section G, Step 6(B).

If Yes to any of the above – Explain:

12) If answers to questions 7 – 11 are acceptable continue to Section D.

¹Obtained from the Hazardous Waste Handling Facility's webpage.

APPENDIX L. Hazardous Waste Handling Facility peroxide forming chemicals evaluation form.



Sandia National Laboratories

RF 2042-PFC (0609, Rev. 0)

D. Analytical (for PFCs – but not Organic Peroxides):

13) Has POC approved the lab space for this procedure? Yes No
If No – Explain: _____

14) Is Safety Equipment present in lab or immediately available?

Safety Shower: Yes No

Spill Kit: Yes No

Fire Extinguisher: Yes No

If No to any of these questions, do not proceed.

15) PPE Worn:

Standard Level D: Yes No

Face Shield: Yes No

Butyl Rubber Gloves: Yes No

Butyl Rubber Apron: Yes No

16) Ventilation Used:

Fume Hood Present and Operational: Yes No

Other: _____

17) Brand of Test Strip Used: _____ Expiration Date: _____

18) Followed procedure outlined in Section G below? Yes No

If No – Explain: _____

19) Result in ppm: _____

Result is less than, or equal to, 80ppm? Yes No

If Yes - The chemical is acceptable for disposal.

If No - This bottle may pose a safety hazard.

The chemical cannot be accepted by the HWMF for disposal.

Have Generator contact HWMF Site Coordinator or HWMF Chemist.

E. Signatures:

Team Member

Name: _____

Signature: _____

Team Member

Name: _____

Signature: _____

Team Member

Name: _____

Signature: _____

Date Tested: _____

APPENDIX L. Hazardous Waste Handling Facility peroxide forming chemicals evaluation form.



Sandia National Laboratories

RF 2042-PFC (0609, Rev. 0)

F. Instructions:

This form is to be used in accordance with AOP 08-02, *Hazardous Waste Characterization, Profiling, and Shipment*; and FOP 08-11, *HWMF Open Container Operations*. This form must be used to document evaluations of Organic Peroxides and Peroxide Forming Compounds (PFCs). Compounds that pass this evaluation are acceptable for disposal through the HWMF.

Section A

Questions must be filled out prior to visiting the site.
POC must be present throughout the Evaluation.

Section B

Questions 1-3, must be completed prior to Site visit.
Questions 4-6, can be completed prior to Site visit based on WDDR, CIS, or the generator.

Section C

Begin by verifying Section A and B information when you arrive at the Site.
Question 7 can be answered prior to the Site Visit based on generator knowledge.
Remaining questions should be filled out at the Site, as indicated on the Form.

Section D: **Note: Section D does not apply to the evaluation of Organic Peroxides.**

Do not perform analytical unless the POC has given approval.
Do not perform analytical unless proper PPE is available and worn.
Do not perform analytical unless proper Safety Equipment is available and used.
Do not perform analytical unless proper LEV is available and used.
WaterWorks Brand Test strips are currently approved for use.

G. Peroxide Test Procedure

To use the WaterWorks Brand test strips, follow these steps:

- 1) Complete Sections A, B and C, of RF 2042-PFC.
- 2) Don the PPE required by Section D.
- 3) Verify Safety Equipment required by Section D.
- 4) Perform work using LEV required by Section D.
- 5) Lower the fume hood sash (if present), so that the barrier is between the bottle opening & your body & face.
- 6) Slowly open the container and remove the lid.
 - A) Examine the lid and mouth of the bottle for the presence of crystals.
 - B) **If crystal formation is observed:**
 - i) Immediately Stop Work.
 - ii) Set the cap carefully inside the fume hood.
 - iii) Lower the fume hood sash completely and turn it off.
 - iv) Notify the Point of Contact, Lab Occupants, and the HWMF Site Coordinator or HWMF Contractor Site Manager.
 - C) If no crystals are observed continue to Step 7.
- 7) Immerse the end of the test strip in the chemical for about 1 second (wet the indicator portion of the strip).
- 8) Remove the test strip and allow the chemical to evaporate to dryness inside the hood.
- 9) Replace the lid and securely close the container.
- 10) Spray a small amount of deionized water on the test strip from the sprayer.
- 11) Allow at least 1 minute for the color to stabilize on the test strip.
- 12) Compare the test strip color to the color chart:
 - No change, or yellow to pale green-blue color, indicates a low concentration of peroxide in the sample. Samples that are less than 80 ppm are acceptable for disposal through the HWMF. The container passes the test.
 - **A blue color** indicates a high concentration. Samples that are **80 ppm** or more, **FAIL** the test, and are not acceptable for disposal at the HWMF.
- 13) Mark the results on the bottle. Also initial, date, and indicate "HWMF" on the bottle.

APPENDIX M. HAZARDOUS WASTE HANDLING FACILITY FOP 08-11.¹

Hazardous Waste Management Facility (HWMF) Open Container Operations

FOP 08-11
Rev. 01
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SANDIA NATIONAL LABORATORIES NEW MEXICO

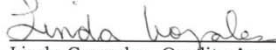
HAZARDOUS WASTE MANAGEMENT FACILITY (HWMF)

OPEN CONTAINER OPERATIONS FOP 08-11, REVISION 01

Replaces: FOP 08-11, Revision 00, Dated October 6, 2008

Effective Date: 10/7/11

Author:



Linda Gonzales, Quality Assurance Program
Project Leader

9/28/11

Date

Reviewed By:



Ken Tetreault, Contractor Manager

9-28-11

Date



Angel Ripoll, HWMF Technician

09-28-11

Date



Tony Mocado, HWMF Technician

9-28-11

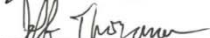
Date



Erik Martinez, HWMF Technician

9-28-11

Date



Jeff Thoroman, IH Customer Support Team

9-29-11

Date



Terri Wallis, SE Customer Support Team

9-29-11

Date

Approved By:



Pamela Puissant, Acting Department Manager

9/28/11

Approval Date

¹Obtained from the Hazardous Waste Handling Facility's webpage.

APPENDIX M. Hazardous Waste Handling Facility FOP 08-11.

Hazardous Waste Management Facility (HWMF) Open Container Operations

FOP 08-11
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ATTACHMENTS

- 1 – Guidelines When Using Respiratory Protection
- 2 - Change History - Revision 00 to 01

FORMS:

[RF 2042-FAF](#), Hazardous Waste Management Facility Fingerprint Analysis Form

[RF 2042-HPL](#), HWMF Pump Usage Log

[RF 2042-PFC](#), Hazardous Waste Management Facility (HWMF) Organic Peroxide and Peroxide Forming Chemicals Evaluation Form

[RF 2042-UIF](#), Hazardous Waste Management Facility Unknown Identification Form

[SF 2001-COC](#), Contract Laboratory Analysis Request and Chain of Custody

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1.0 PURPOSE, SCOPE AND OWNERSHIP

1.1 Purpose

This Sandia National Laboratories/New Mexico (SNL/NM) field operating procedure (FOP) describes the handling of open waste containers by Regulated Waste and Pollution Prevention Department (RWPPD) personnel. This FOP provides specific instructions and general guidance to RWPPD personnel, primarily HWMF Technicians.

1.2 Scope

This FOP contains the requirements for handling open waste containers. This FOP is relevant to RWPPD personnel who perform work under this procedure. These personnel shall read this FOP and acknowledge understanding by signing the [RF 2042-AUL](#), Authorized Users List (AUL).

1.3 Ownership

The author is responsible for the structure and content of this FOP. Recommendations for improvement and comments regarding the modification of this procedure should be forwarded to the Department Manager or the author.

1.4 Frequency of Review

The activities covered by this procedure are considered “Medium” risk and therefore this procedure will be reviewed every two years.

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2.0 RESPONSIBILITIES

2.1 HWMF Personnel

All HWMF Personnel are responsible for the following:

- Reading and following work practices specified in this and other HWMF technical work documents (TWDs).
- Stopping work if unsafe work conditions exist.
- Ensuring that training and qualifications are current.
- Knowing evacuation plans, evacuation routes, building alarms, and the HWMF Contingency Plan.
- Being familiar with locations of eyewashes, safety showers, fire extinguishers, and spill containment equipment.
- Being familiar with spill control measures at the HWMF.

2.2 Department Manager

The Department Manager is responsible for the following:

- Approving the content of this FOP.
- Ensuring that HWMF operations are adequately staffed and funded.
- Delegating management of the HWMF to the HWMF Project Leader and HWMF Site Coordinator.
- Notifying management and the DOE Facility Representative of emergencies and/or incidents as required by the [OOPS](#) reporting process.
- Ensuring training requirements are met.

2.3 HWMF Project Leader

The HWMF Project Leader is a member of HWMF Supervision. The HWMF Project Leader is responsible for the following:

- Providing programmatic oversight.
- Ensuring compliance with this FOP.
- Authorizing personnel to work at the HWMF.
- Ensuring training requirements are adequate.

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2.4 HWMF Site Coordinator

The HWMF Site Coordinator is a member of HWMF Supervision. The HWMF Site Coordinator is responsible for the following:

- Overseeing daily operations at the HWMF.
- Periodically verifying HWMF personnel have completed required training.

2.5 Contractor Manager

The Contractor Manager is a member of HWMF Supervision. The Contractor Manager is responsible for the following:

- Supervising daily operations at the HWMF.
- Ensuring contract employees possess the proper training and qualifications.
- Ensuring contract employees are entered in the Medical Monitoring Program in accordance with Occupational Safety & Health Act (OSHA) [29 CFR 1910.120\(f\)](#).
- Ensuring that PPE of the right type and size is available to HWMF personnel and in a readily accessible location.

2.6 Field Chemist

The Field Chemist is responsible for the following:

- Coordinating sampling activities.
- Briefing HWMF Technicians on the hazards associated with the sampling activity.
- Supporting the characterization determination.

2.7 HWMF Technicians

HWMF Technicians are responsible for the following:

- Using PPE specified for job assignments.
- Knowing the locations and proper uses of eyewashes, safety showers, fire extinguishers, and spill containment equipment.
- Knowing spill control measures at the HWMF.
- Performing open container operations.

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2.8 Administrative Coordinator

The Administrative Coordinator is responsible for ensuring records generated by this FOP are properly managed.

2.9 Sample Management Office (SMO)

The Sample Management Office (SMO) provides centralized management of samples and analyses performed by contract laboratories. The SMO provides technical and administrative support for environmental programs' sampling and analysis initiatives. The primary objective of the SMO is to ensure that analytical data is of adequate technical quality and content to meet the data quality and program requirements. The SMO QA processes and procedures are developed and maintained to ensure that deliverables are compliant and meet customer requirements. The SMO Quality Assurance Project Plan (SMO QAPP) meets DOE, EPA, and SNL Program QA requirements. The following are support functions performed by the SMO:

- Procure contracts with analytical laboratories using a detailed technical statement of work.
- Monitor data deliverables (both hardcopy and electronic) for compliance with contract and program requirements.
- Conduct laboratory oversight through audits, assessments, and data review.
- Manage both technical and financial contractual requirements.
- Provide sample packaging management services.
- Provide assistance with sampling documentation and manage the Chain of Custody process.
- Act as a liaison between each customer and the contract laboratory.
- Manage sample information and database maintenance for sample tracking and analytical results.
- Provide data management and QC of all electronic analytical data.
- Coordinate and provide guidance for sampling strategies and procedures.
- Provide data validation through third party independent off-site contractor consultants.

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3.0 TRAINING REQUIREMENTS

The safe handling of waste relies heavily on the training and qualification of the personnel performing the work. All activities described in this FOP are performed by personnel who meet the qualification and training requirements for their job titles, as specified in the current revision of the RWPPD Training Tracking Systems.

3.1 Authorized Users List

HWMF personnel who perform the activities described in this procedure read this FOP and sign an Authorized Users List (AUL). Two AULs are maintained as controlled documents. One is maintained by the Administrative Coordinator for contractor employees. A second AUL is maintained by training personnel for Sandia employees.

4.0 PPE & SAFETY

Open container operations can include verifying or ascertaining the characteristics of the waste that is being managed and transferring compatible chemicals together into one container. Open container activities present risks that differ in type and extent from the risks posed by other activities performed at the HWMF.

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4.1 PPE

Open container operations described below require HWMF Technicians to wear Standard Level-D PPE. Where the PPE requirements differ from this standard, there is a section that describes what the specific PPE requirement entails.

Standard Level-D PPE consists of the following:

- Cloth coveralls
- ANSI-approved safety glasses with side shields or safety glasses with built-in side protection (prescription if necessary)
- Safety footwear
- Abrasion-resistant leather or neoprene heavy cotton gloves
- Nitrile or polyvinyl chloride (PVC) disposable gloves

4.2 Respiratory Protection

Personnel may decide to use respiratory protection for certain open container operations. Respiratory protection is not currently required as identified by Industrial Hygiene personnel in an ES&H Evaluation. If activities change, Industrial Hygiene personnel will be contacted for further evaluation. When respiratory protection is utilized, the requirements of [ESH100.2.IH.3](#), *Control Inhalation Hazards Using Respiratory Protection*, will be followed. In addition, see Attachment 1, *Guidelines When Using Respiratory Protection*.

4.3 Safety

Procedures to minimize hazards during open container operations include the following:

- Ensure that local exhaust ventilation systems and respiratory protection equipment are working properly when used.
- Containers shall be opened and sampled individually in a segregated, adequately ventilated, and illuminated area.
- Personnel will be experienced in using approved methodologies for sampling hazardous wastes, such as those listed in [40 CFR Part 261, Appendix 1](#), *Identification and Listing of Hazardous Waste* and those found in [SW-846](#), *Waste-Hazardous Waste-Test Methods*.
- Open container operations will be conducted by a minimum of two qualified personnel.
- Containers will be positioned so that the bung, if present, is up.

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- HWMF Supervision is to be notified immediately if any unusual conditions associated with any container are observed. This would include visible signs of deterioration, signs of pressurization (bulging), unusual fittings, or crystallization around the bungs.
- Non-sparking tools will be used to open drums.
- Personnel must know the locations of telephones, emergency phone numbers, eyewash equipment, safety showers, fire extinguishers, and other emergency equipment prior to conducting open container operations.
- Personnel will remove PPE that becomes contaminated as soon as practicable.
- Personnel will not open containers of waste that are shock sensitive or capable of forming peroxides prior to consulting HWMF Supervision.
- Do not use organic materials; i.e., paper or cloth rags when handling or sampling acids or oxidizing materials.

4.4 Opening Containers

Prior to opening a container, HWMF Technicians will:

- Don Standard Level-D PPE.
- Inspect containers for physical defects or abnormalities including the following:
 - Deterioration, corrosion, positive pressure (bulging), negative pressure (concave), exotic drum, or unusual fittings.
- Visually inspect for crystalline material around bungs or openings.

CAUTION: *Do not attempt to move or open containers with crystalline material around their openings; this material may indicate potentially explosive contents!*

- If any abnormal conditions are noted, contact HWMF Supervision for further instructions.
- Ensure that personnel in the area know that open container operations are being conducted.
- Ensure spill clean-up equipment is readily available.
- Position containers to facilitate emergency egress.
- Once containers are in place, ground metal drums and containers, as necessary.
- Cover container tops with spill pads as necessary to avoid contaminating container exteriors

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4.5 Closing Containers

Once the open container operation has been completed, HWMF Technicians shall adhere to the following requirements:

- Reseal drum/container openings as soon as practical. If an open drum/container cannot be resealed, arrange for the contents to be transferred to another container.
- Decontaminate all contaminated reusable equipment; e.g., pumps and respiratory protection.
- Collect, package, and label as solid or hazardous waste all contaminated non-reusable items such as plastic sheeting and rags for disposal.
- Return the work area to pre-operation conditions.
- Remove PPE.

4.6 Waste

All waste generated in the open container process must be collected and managed in compliance with [ESH100.2.ENV.22](#), *Manage Hazardous Waste at SNL/NM*.

5.0 WASTE TYPES THAT MAY BE SAMPLED

An example of the types of wastes that HWMF personnel sample are:

- Laboratory Chemical Wastes
- Process Chemical Wastes
- Unknown Wastes
- Other: Spill clean-up, contaminated soil, per TSDF requirements, PCBs, and other waste as identified by the Field Chemist

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5.1 Laboratory Chemical Wastes

Laboratory chemical wastes are defined in the RCRA Part B Permit as waste produced during various research, development, and testing operations, including:

- Excess or residual reagent chemicals.
- Off-specification or expired chemicals, such as paints or photographic chemicals.
- Chemical solutions or mixtures of known composition prepared by chemists for various research projects.
- Solid laboratory waste, such as laboratory wipes contaminated with solvent or lead solder.

These wastes are typically generated from multiple sources in small quantities at infrequent intervals. Sampling and analysis is not typically required for these types of wastes because knowledge of process is sufficient to determine the hazards associated with handling and storage of the waste and the requirements and restrictions for disposal.

In cases where the knowledge of process is not sufficient to determine the hazards associated with handling and storage of the waste and the requirements and restrictions for disposal, additional information must be collected about the waste.

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5.2 Process Chemical Wastes

Process chemical wastes are defined in the RCRA Part B Permit as coming from sources that consistently produce certain waste streams throughout the year, usually in relatively large volumes. The RCRA Part B Permit specifically identifies the following categories of process chemical wastes that may be generated at SNL:

- PCB Waste: This waste consists of transformer oils from transformers produced prior to 1978. This waste does not include waste from clean-up activities such as soil that may be contaminated with PCBs because clean-up activities are not considered a “process” that controls the chemical characteristics of the waste stream.
- Plating Waste: This waste consists of concentrated and dilute acids or caustics containing dissolved or precipitated metals generated during routine plating operations.
- Circuit Waste: This waste consists of rinse and cleaning solvents, such as degreasing solvents and wastes containing metal contaminants from solders used in the routine production of printed circuits. This waste stream also consists of concentrated and dilute acids and caustics containing dissolved or precipitated metals used in the routine production of printed circuits.
- Vehicle Maintenance Waste: This waste consists of oils, coolants, and degreasing solvents possibly contaminated with lead or other metals generated from routine vehicle maintenance.
- Thermal Treatment Facility Waste: This waste consists of ash contaminated with metals from the routine incineration of explosive waste in the Thermal Treatment Facility.
- Photo Developing Waste: This waste consists of photo developing chemicals, such as fixers, developers, and replenishers that may be acidic or basic and contaminated silver that is generated during routine photo developing.
- Semiconductor Waste: This waste consists of acids and solvents used for cleaning during the routine fabrication of semiconductors.

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In addition to the process waste described in the RCRA Part B Permit, SNL may generate other waste that could be considered process chemical waste. The definition of process waste in the RCRA Part B Permit is not specific; therefore, the following criteria have been developed for identifying new process chemical waste streams produced at SNL:

- The waste must be non-laboratory chemical waste.
- The waste must be generated from a routine maintenance or production process conducted by a single generator (e.g., a process that follows an established procedure that generates a chemical waste).
- The waste must be RCRA regulated.
- The routine process must generate a minimum of 30 gallons of waste per month.

The categories of process chemical waste identified in the RCRA Part B Permit and the associated waste streams generated at SNL that fall within the categories are maintained in the HWMF operating record. In addition, the other waste streams that meet the criteria listed in the bullets above are maintained in the HWMF operating record.

The RCRA Part B permit requires detailed analytical testing to be conducted on 5 percent of the containers received from each defined, regularly received process chemical waste stream. The process to ensure that testing is conducted is described in [AOP 08-02](#), *Hazardous Waste Management Facility (HWMF) Waste Characterization, Profiling, and Shipment*.

5.3 Unknown Wastes (Controlled Location)

If an unknown is discovered in a controlled location, the unknown waste may be considered “unknown waste (controlled location)”. If an unknown is found outside a controlled location, the unknown is considered “unknown waste (uncontrolled location)” and will be handled by the EOC.

If the unknown waste (controlled location) is 20 gallons or less, the HWMF will provide support for analysis. If the waste is over 20 gallons, the generator will be responsible for analysis. A WDDR submitted as an unknown waste (controlled location) shall have been surveyed and be determined not to be radioactive, be “natural occurring radioactive material (NORM)” or be exempt from regulation. Evidence of an evaluation for beryllium contamination shall also be provided.

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6.0 SAMPLING ACTIVITIES

6.1 Fingerprint Checks

Process chemical wastes that arrive in containers larger than 30 gallons must have a fingerprint check completed. The fingerprint check process may be used on other containers.

Perform fingerprint checks as follows:

- Use LEV during the fingerprint check.
- Collect fingerprint information on the contents of the container that includes one or more of the following parameters:
 - Physical state (solid, liquid, gas, sludge)
 - pH
 - Oxidation potential (for inorganic liquids)
 - Color
- Document the results of the fingerprint checks on [RF 2042-FAE](#), *Hazardous Waste Management Facility Fingerprint Analysis Form*.
- Provide [RF 2042-FAE](#) to the Administrative Coordinator.
- Containers of used oil that will be recycled shall be fingerprinted for chlorinated compounds.

6.2 Generator Site Examination of Organic Peroxides and Peroxide Forming Compounds (PFCs)

When identified by the Field Chemist, prior to acceptance for disposal, certain Organic Peroxides and PFC waste must be examined at the generator site.

- Examination of PFCs is performed by a team of at least two HWMF personnel.
- Visual examination can be performed using Standard Level-D PPE.

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- When testing for peroxide formation in PFCs, Standard Level-D PPE will be supplemented with:
 - Face Shield
 - Butyl Rubber outer gloves
 - Butyl Rubber Apron
- When testing for peroxide formation, use LEV or a fume hood.
- Document the examination on [RF 2042-PFC](#), *Hazardous Waste Management Facility (HWMF) Organic Peroxide and Peroxide Forming Chemicals Evaluation Form*. [RF 2042-PFC](#) contains instruction on how to conduct the examination.
- Prior to the examination, the Field Chemist will fill out the [RF 2042-PFC](#) to the extent possible, based on discussions with the generator and any information provided as part of the WDDR.
- Prior to the examination, the Field Chemist will brief the team on the known and suspected conditions of the Organic Peroxides or PFCs.
- Site examination must be performed in the presence of the designated Point of Contact (POC).

If the examination team tests for peroxide formation, they will use one of the approved test strips identified in the instructions to [RF 2042-PFC](#), and follow the procedure described therein.

6.3 Unknowns

HWMF personnel utilize three methods in sequential order, as necessary, to identify the unknown waste. These methods are:

- 1) Generator Site Visual Examination
- 2) HazCat Analysis
- 3) Detailed Off-Site Analytical Testing

Generator Site Visual Examination and HazCat Analysis are performed by HWMF personnel. For detailed analytical testing, HWMF will collect a sample of the waste in compliance with Sample Management Office (SMO) processes and procedures, and send it to the SMO for submittal for analysis.

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6.3.1 Generator Site Visual Examination

Generator site visual examination is performed by a team of two HWMF personnel (one being HazCat trained). Prior to proceeding to the generator's location:

- The Field Chemist will notify personnel at Building 928 that HazCat Analysis may be performed in the fume hood.
- Obtain the following:
 - A copy of the Open flame Hot Work Permit.
 - HazCat kit and a propane cylinder.
 - Faceshields or safety glasses with side shields.
 - Verification that a radiation survey was performed and the unknown was determined not to be radioactive, be NORM or exempt from regulation.
- Proceed to the generator's site in a transportation vehicle that does not contain other waste.

This team examines the chemical for various properties, such as:

- Physical state
- Color
- Age
- Storage and container conditions
- Changes in substance
- Phase separations
- Quantity of chemical
- Any labeling

In addition, the team will observe the type of operations in the nearby area and interview personnel associated with the laboratory/area where the unknown is located. This information is documented on the [RF 2042-UIF](#), *Hazardous Waste Management Facility Unknown Identification Form*.

- Affix a temporary P# on the waste package.
- Place the unknown waste into a secondary container and place a "Sample" label on the outside of the container.
- Transport the unknown waste to Building 928, in compliance with [FOP 06-03](#), *Hazardous Waste Pickups*, as a sample.

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6.3.2 HazCat Analysis

HazCat analysis is performed by personnel who are trained in the HazCat analysis process. The HazCat process is as follows:

- Prepare for HazCat analysis.
 - Post a copy of the Open Flame Hot Work Permit in a conspicuous location near the fume hood until the operation is completed.
 - Verify that the fume hood is operational.
 - Determine who will be the operator and who is designated as the fire watch.
 - Check that the fume hood is free of chemicals prior to placing the unknown waste into the fume hood.
 - Ensure the fire extinguisher in Building 928 on the east wall is charged.
 - Complete the pre-hot work check prior to performing the HazCat Analysis.
- Remove the unknown waste package from its secondary container and place in the fume hood.
- Open the unknown waste package, and using the equipment from the Hazcat toolkit, remove a sample of the waste.
- Close the unknown waste package and return it to the secondary container.
- Repeat the process to obtain a sample if there is more than one package.
- Place an empty bag in the fume hood designated for test generated waste (e.g., used wipes) resulting from the testing process.
- Don additional PPE if required: Face shields will be worn if igniting a sample.
- Perform the tests using HazCat procedures for each of the samples. Complete the tests for one sample at a time.
- Document the results of the HazCat testing on [RF 2042-UJF](#).
- Based on the results determine what the unknown is.

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- If the waste cannot be identified, detailed analytical testing by an analytical laboratory may be required. If so, obtain a sample and process per Section 6.4, Detailed Analytical Testing by an Analytical Laboratory.
- When all the samples have been tested, take one of the unknown waste packages out of the secondary container and place it in the fume hood.
- Place the associated unused samples and sample containers in the unknown waste package.
- Continue the previous actions until all the leftover samples and used sample containers have been returned to the waste packages. Ensure the waste packages are in secondary containers with the lids securely closed.
- Remove the test generated waste and dispose of it according to Sandia policy.
- Remove the HazCat test equipment and return it to the HazCat kit. Take the HazCat test kit and return it to its storage location.
- The Operator will take [RF 2042-UIF](#) to the Field Chemist for processing.
- The Hot Work Permit can be removed at this time. The Fire Watch will remain with the unknown waste and complete the Hot Work Permit.
- If the unknown waste is identified, upon completion of the classification process, new P#s will be generated and provided to the HWMF Technicians.
- HWMF Technicians will place the new P#s over the temporary P#s and follow [FOP 06-03, Hazardous Waste Pickups](#), to pickup and deliver the known waste to the HWMF for processing.
- If the waste is not identified and requires detailed analytical testing, the HWMF Technicians will be directed to return the unknown waste to the generator.

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6.4 Detailed Analytical Testing by an Analytical Laboratory

The SMO provides centralized management of samples and analysis performed by contract laboratories. The SMO is considered a “Compliance Partner”. The SMO provides technical and administrative support services for sampling and analysis activities. The primary objective of the SMO is to ensure that analytical data is of adequate technical quality and content to meet customer data quality and project requirements.

Samples will be collected and managed according to the following SMO procedures:

- [LOP 94-03](#), *Sample Handling, Packaging and Shipping*
- [AOP 95-16](#), *Sample Management and Custody*

The following is a general description of the process:

- Obtain unique control numbers (e.g., ARCO #) from the [SMO website](#).
- Work with SMO personnel to determine what Analytical Laboratory should be used.
- Start the process by entering “New Bottle Orders” on the [SMO website](#).
- When sampling is needed, complete [SF 2001-COC](#), *Contract Laboratory Analysis Request and Chain of Custody*.
 - Under the section titled “Sample Location Detail”, enter unique information that ties the sample to the waste/material being sampled (e.g., P#, DR#, etc.)

When collecting samples of waste for detailed analytical testing, sampling personnel shall adhere to the following general requirements:

- Use LEV during sampling (use fume hood for small containers). Respiratory protection may be used. Note: For sampling of waste oils LEV or respiratory protection is not required.
- During sampling, keep personnel at a safe distance from containers being opened.

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7.0 WASTE TRANSFER OF LIQUIDS

7.1 Bulking, Pouring-Off, or Pumping

The following sections describe the process of transferring liquids to new containers by bulking, pour-off, or pumping.

Liquids that are brought to the HWMF in reusable containers need to be transferred into approved shipment containers before they are shipped. After transfer, the reusable containers can be returned to the generator. In some cases liquid wastes are accepted at the HWMF that can be combined together in order to facilitate ease of shipment or reduce disposal costs.

Both of these processes must be performed in Building 959, and require the use of specialized ventilation equipment. Respiratory protection is not required but optional. Because of the specialized nature of these operations, detailed PPE requirements are described below, along with detailed instructions.

For bulking of oils, no LEV or respiratory protection is required. The supplemental PPE in Section 7.3 is not required. Barriers are not required.

7.2 Prerequisites

Observe these prerequisites before performing transfer activities:

- Perform transfer operations only in Building 959.
- Ensure that all casual personnel leave the building before transfer begins.
 - Use barriers (chains, portable barriers, tape, etc.) to mark the building off-limits during transfer.
- Maintain at least a three-foot aisle space, with access to exits at all times.
- If not transferring over the sump or if transfer operations cover an area larger than that of the sump, ensure adequate secondary containment is used. Use of a drum spill pallet is acceptable.
- Place sorbent pads on the tops of collection containers to keep contents from contaminating drum exteriors. If sorbent pads become contaminated, manage in accordance with Section 7.6.
- Ensure drum contents and compatibility of materials to be transferred before opening waste containers.

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- Ensure compatibility of wastes with collection containers. Consult with a Field Chemist regarding compatibility/suitability concerns.
- Use only new DOT-approved containers as final collection containers, otherwise the container must be overpacked in a DOT-approved container prior to shipment.

7.3 PPE

The PPE requirements for transfer operations include standard Level-D PPE supplemented with:

- Apron
- Dual Nitrile/butyl/vinyl gloves
- Tyvek sleeves
- Operations during extremely hot or cold conditions should be conducted only after consultation with Industrial Hygiene.
- Face shields if not using respiratory protection.
- Use of respiratory protection during bulking and pour-off operations is at the discretion of the user.

CAUTION: *Transfer personnel shall consult HWMF Supervision if they have any concerns or questions about respiratory protection.*

CAUTION: *Unknown materials shall not be transferred.*

7.4 Procedure

- Don supplemental PPE described in Section 7.3.
- For flammable materials, ground the collection container and bond the pump or pouring nozzle of the container being emptied to the collection container with a wire or other conductive material.
- If using a respirator, follow manufacturer's instructions for set-up. See Attachment 1, *Guidelines When Using a Respirator*.
- For small containers the fume hood may be used as respiratory protection.

When transferring, proceed as follows:

- Adjust the exhaust ventilation system to minimize the amount of vapors escaping to the work area. The exhaust ventilation system should be as close to the open waste container opening as is possible, without impeding the work. The ventilation trunk shall be no more than 1 trunk diameter from the waste container opening.

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- Open both bungs of the collection container.
- If pouring off into a 5 gallon container place the 5 gallon container into a 20 gallon drum that is compatible with the LEV attachment.
- If bulking or pouring, insert a compatible funnel into the opening of the collection drum if waste is to be poured into the collection container.
- One HWMF Technician will be responsible for ensuring the ventilation trunk is the correct diameter from the opening of the waste container.
- If pouring off, and if not using the ventilation attachment, the HWMF Technician will also ensure a ventilation trunk is the correct diameter from the opening of the collection container.
- If pumping, attach the stinger to the air line. Ensure the transfer tube is inserted into the collection container and the stinger into the waste container.
- One HWMF Technician will be responsible for waste transfer.
- Open one waste container. If there are two bung openings, open both to facilitate bulking.

CAUTION: *Ensure that only compatible wastes are being bulked into each collection container. Ensure that only one waste stream is bulked at a time.*

CAUTION: *Do NOT use funnels contaminated with organic waste for bulking oxidizing or strongly acidic material. Do NOT leave pumps unattended while in operation. Change any contaminated PPE immediately.*

- Bulk, pour or pump wastes into the collection drum slowly to avoid splashing and overfilling of the drum or funnel.
Note: *If a pump is used for organic liquids, log the date used and the amount of time it is operational (use [RF 2042-HPL](#), HWMF Pump Usage Log). If the pump log shows usage greater than 250 hours for the current year, notify HWMF Supervision.*
- Continue transferring wastes into the collection drum, watching for signs of reaction (e.g., heat, smoke, and turbulence). Immediately leave the area and consult HWMF Supervision if these conditions are observed.
- Empty waste containers into the collection drum.
- Leave at least a 2-inch headspace in the top of all collection drums.
- Do not doff PPE, including respiratory protection until container has been closed.

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7.5 Post Transfer

Once transfer is complete, follow these procedures:

- Replace lids or covers on the collection drum lightly to allow any excess pressure to vent. Tighten lids firmly before moving collection drums to storage areas.
- Doff supplemental PPE.
- Remove the P# bar code from the waste container and adhere it to the collection drum. Note: This can be done prior to transfer.
- When the waste container is empty, the waste container may be crushed (See [FOP 06-03, Hazardous Waste Pickups](#)) if non reusable. Empty drums that contained acute hazardous waste shall be returned to Building 959. Notify HWMF Supervision when this occurs.
- Affix a white “Empty” sticker to empty reuseable containers (e.g. “safety cans”) and store these containers inside near the front of Building 959 until they can be returned to the waste generator for reuse.
- Decontaminate non-disposable equipment. Dispose of contaminated disposable equipment in accordance with Section 7.6.
- Clean and disinfect respiratory equipment if used.
- Remove barrier, if used.

7.6 Waste

Waste generated in the bulking activity shall be managed as follows:

- Potential hazardous wastes generated in this activity include contaminated equipment and materials, contaminated PPE, empty containers with hazardous waste residues, and decontamination residues.
- Wastes must be handled in accordance with [ESH100.2.ENV.22, Manage Hazardous Waste at SNL/NM](#), and in accordance with HWMF procedures.
- Items contaminated with acutely hazardous waste shall immediately be segregated, packaged, and labeled as determined by a Field Chemist.

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8.0 RECORDS

Records are managed in accordance with Department and Corporate procedures.

9.0 REFERENCES

[AOP 95-16, Sample Management and Custody](#)

[FOP 06-03, Hazardous Waste Pickups](#)

[ESH100.2.IH.3, Control Inhalation Hazards Using Respiratory Protection](#)

[ESH100.2.ENV.22, Manage Hazardous Waste at SNL/NM](#)

[LOP 94-03, Sample Handling, Packaging and Shipping](#)

[Site-wide Contingency Plan for Resource Conservation and Recovery Act - Regulated Waste Management Units, Appendix E, General Part B Permit Application, Sandia National Laboratories/ New Mexico](#)

[Contingency Plan for the Hazardous Waste Management Facility](#)

[29 CFR 1910.120\(f\), Hazardous waste operations and emergency response](#)

[40 CFR Part 261, Appendix 1, Identification and Listing of Hazardous Waste](#)

Sandia National Laboratories RCRA Part B Permit

[SW846, Waste-Hazardous Waste-Test Methods](#)

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Attachment 1

Guidelines When Using Respiratory Protection

Set-up

1. Unchain the tanks.
2. Roll the dolly into the Bldg. 959 Lab.
3. Unroll the airline hoses.
4. Obtain the Breathing Air System Manual.
5. Perform the items listed under Setup/Operations.
6. Plug the airline into the Breathing Air System.
7. Plug the airline into the respirator.
8. If the alarm on the Breathing Air System sounds, go through the Setup/Operations section of the Manual again.

Precautions

1. When it is cold, airline may coil causing a tripping hazard.
2. Do not step on the airlines.
3. Try not to cross airlines.
4. If the alarm on the Breathing Air System sounds, proceed to exit.

Shut Down

1. Both workers proceed to the exit door together.
2. Remove the airline from the waist belt.
3. Remove the respirator.
4. Allow the work area to vent approximately 20 minutes.
5. Return and turn off the valves on the air tanks.
6. Remove the airlines, roll the airline hoses, and return to storage.
7. Roll the dolly back to its storage location.
8. Attach the chain around the tanks.

Note: Steps 2 and 3 are interchangeable

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Attachment 2

Change History – Revision 00 to 01

Section	Description of Change
Throughout	The procedure was changed throughout to address current practices and to add more detail to each process.
2.9	Responsibilities of the Sample Management Office (SMO) were added. The SMO will be used to process samples taken by HWMF personnel.
6.3.2	Documented the current process for performing HazCat operations. HazCat operations will not be performed in a fume hood in Building 928.
6.4	Analytical samples will now be processed according to SMO procedures.
7.0	Use of a drum cover was added. Solidification of liquids was removed. This activity is not currently being performed at the HWMF.
Attachment 1	Attachment 1 was added to address the use of respirators and the precautions.

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