Robert J Giraud
<Robert.J.Giraud@US
A.dupont.com>

01/12/04 01:27 PM

To: Rich Leukroth/DC/USEPA/US@EPA, John
Blouin/DC/USEPA/US@EPA, Greg Fritz/DC/USEPA/US@EPA
cc: david.menotti@shawpittman.com, Stephen H Korzeniowski
<Stephen.H.Korzeniowski@USA.dupont.com>, Robert C Buck
<Robert.C.Buck@USA.dupont.com>, bill.beers@omnova.com
Subject: Revised Draft Appendices for Incineration Testing Draft ECA

Colleagues,

Attached are revised drafts of proposed ECA Appendices B.1, D.1, D.2, D.3.,
and C.1 in PDF format based on the Fluoropolymers ECA Drafting Committee
conference call on Jan. 6.

(See attached file: App B.1 TGA Guideline draft 1-12-04.pdf)

(See attached file: App D.1 Exhaust Gas Sampling draft 1-12-04.pdf)

(See attached file: App D.2 PFOA analysis draft 1-12-04.pdf)

(See attached file: App D.3 Wickbold Torch draft 1-12-04.pdf)

(See attached file: App C.1 transport test draft 1-12-04.pdf)

I believe that I have made all the specific changes discussed during that
call. Additionally, I have made the following 2 revisions based on
conversation with Phil Taylor:
    B.1 -- 11.4 -- corrected lower end of available weight range for TGA
    specimen
    C.1 -- p. C.1-1, L39-41 -- added brackets in part of the parenthetical
    expression for clarification

As suggested, the additions and deletions are clearly marked in the
attached documents above.

Greg, all "Notes" in Exygen method not addressed in revised D.2 above are
still to be understood as notes in the method.

Please note that I am still hoping to hear feedback from other company
technical representatives on the above draft documents.

I have requested fluoropolymers technical person for Tuesday afternoon
call, but I am not sure of his availability.

I am still working on revisions to C.2 based on the call and on the other
things that I owe.

I look forward to our discussions on Tuesday.

Best Regards,

Robert

P.S. Rich, please use the printer that John and Greg use to print this to
assure that spacing between words comes thru OK.   I am still trying to
learn more about WordPerfect so that I can convert these to WPD.

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App B.1 TGA Guideline draft 1-12-04.| App D.1 Exhaust Gas Sampling draft 1-12-04

App D.2 PFOA analysis draft 1-12-04. App D.3 Wickbold Torch draft 1-12-04. App C.1 transport test draft 1-12-04.|

APPENDIX B.1
GUIDELINE FOR THERMOGRAVIMETRIC ANALYSIS

ASTM E 1868-02 "Standard Test Method for Loss-On-Drying by
Thermogravimetry" will be used as the guideline for conducting
the analysis described in Appendix C.2.3 with the following
~~exceptions~~modifications for this testing program:

Section	~~Exception~~Modification
2.1	• Standard practices at the University of Dayton Research Institute (UDRI) may be used as references throughout the standard in place of the ASTM standards noted in this section.
4.1	• The loss-on-drying ~~(LOD)~~ value specified in the second through fifth sentences of this section will not be recorded.
7.1.3	• The programming rate of the furnace will be set at 10 to 25°C/min, rather than 5°C/min. Pursuant to section 11.6, the temperature program rate will be documented in the report. • The isothermal temperature within the range of 25 to 1000°C will be maintained ±3°C, rather than ±2°C.
7.1.4	• The specimen atmosphere control system will be capable of supplying dry air in addition to "inert dry gas (usually purified grade nitrogen)".
7.1.7	• The temperature program rate will be set at 10 to 25°C/min, rather than 5°C/min. Pursuant to section 11.6, the temperature program rate will be documented in the report. • The temperature program rate will be controlled to within the range of ±3°C/min, rather than ±0.1°C/min. • Within the range of 25 to 1000°C, the isothermal temperature will be maintained within ±3°C, rather than ±2°C.
11.4	• The mass of the test specimen noted in the first sentence of this section will be 0.~~05~~005 to 5 mg, rather than 10±1 mg (i.e., 9 to 11 mg).
11.6	• The test specimen heating rate will be set at 10 to 25°C/min, rather than 5°C/min noted in the first sentence of this section. Pursuant to section 11.6, the temperature program rate will be documented in the report.
11.9	• Termination criteria will follow Test Method A as

	outlined in section 11.10.1.
11.10.1	• The "fixed period of test time" ~~noted~~ mentioned in this section will be set at 5 min.
11.10.1.1	• ~~LOD~~ Loss-on-drying values will not be recorded.
12.1	• The ~~LOD~~ loss-on-drying value will not be calculated.
13.1.1	• The "identification and description of the material being tested" will be consistent with the information known to the analyst.
13.1.5	• The ~~LOD~~ loss-on-drying value will not be included in the report.
14.2	• This section is not applicable because the Test Method A termination criteria will be used.

Reference
ASTM E 1868-02 "Standard Test Method for Loss-On-Drying by Thermogravimetry", ASTM International. For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

1 **APPENDIX C.1**
2 **PFOA TRANSPORT TESTING**
3
4 C.1.1 Significance
5
6 Testing will be performed to verify that potential PFOA
7 emissions from the combustion testing described in Appendix
8 C.2 can be quantitatively transported from the high
9 temperature reactor into the exhaust gas sampling apparatus
10 (aqueous solution bubblers).
11
12 Acceptable PFOA transport will be demonstrated if the
13 transport efficiency (as computed in one or more of the
14 formulas below) is greater than or equal to 70%.
15
16 C.1.2 Experimental Plan
17
18 C.1.2.1 Base Plan
19
20 Transport of PFOA across the laboratory-scale thermal
21 reactor system described in Appendix C.2.4 and into the
22 exhaust gas bubblers described in Appendix D.1 will be
23 quantitatively determined as an indication of transport
24 from the high temperature reactor into the bubblers.
25
26 A PFOA standard of known purity greater than or equal to
27 97% will be gasified at 150 to 250 °C (based on
28 thermogravimetric analysis of PFOA) with transfer line and
29 reactor temperatures 0 to 100 °C higher than the
30 gasification temperature.
31
32 Three replicate transport efficiency test runs will be
33 conducted. A minimum of one blank run will be conducted
34 prior to each transport efficiency test run.
35
36 The sample size of the PFOA standard to be gasified will be
37 less than 5 mg. The reactor exhaust gas will be collected
38 into bubbler aqueous solution as described in Appendix D.1
39 (including an HPLC water rinse of the flexible tubing [used |
40 to connect the thermal reactor system and the bubbler
41 assembly] into the aqueous solution composite), which will |
42 be analyzed for PFOA as described in Appendix D.2. In
43 order to provide a second way of demonstrating quantitative
44 transport, this aqueous solution composite will also be
45 analyzed for total fluorine as described in Appendix D.3.
46 (Testing for total fluorine is included due to possibility
47 of thermal degradation of PFOA under transport test

C.1-1

1 conditions.) Therefore, for this transport testing the
2 sample size of PFOA standard will be sufficiently high to
3 assure that the total fluorine input to the thermal reactor
4 system will be greater than 140% of the mass corresponding
5 to the limit of quantitation (LOQ) for total fluorine in
6 the aqueous solution composite. (The LOQ for total
7 fluorine in aqueous solution is much higher than the LOQ
8 for PFOA in aqueous solution.)
9
10 The amount of PFOA and total fluorine in the thermal
11 reactor system exhaust gas will be determined via analysis
12 of the aqueous solution composite as noted above.
13
14 The amount of PFOA fed to the thermal reactor system will
15 be known based on measurement prior to gasification and
16 will be verified by weighing the pyroprobe insert cartridge
17 before and after each test run. The amount of fluorine fed
18 to the system will be calculated from the amount of PFOA
19 fed, the known purity of the PFOA, and the known fluorine
20 fraction of the PFOA standard.
21
22 PFOA transport efficiency (TE) as a percentage will be
23 computed as follows:
24
25 % PFOA TE = mass of PFOA in aqueous solution composite * 100   (1)
26   mass of PFOA fed to thermal reactor system
27
28 Total fluorine (TF) transport efficiency as a percentage
29 will be computed as follows:
30
31 % Total F TE = mass of total F in aqueous solution composite * 100 (2)
32   mass of total F fed to thermal reactor system
33
34 C.1.2.2 Contingent Testing
35
36 If the transport efficiencies for both PFOA (equation 1)
37 and total fluorine (equation 2) are less than or equal to
38 70%, then additional work will be performed. ~~as described~~
39 ~~in Section C.1.2.2.~~
40
41 ~~C.1.2.2 Contingent Testing~~
42
43 ~~As indicated by Section C.1.2.1,~~ This additional work will
44 be performed~~, as necessary,~~ in a step-wise fashion to
45 determine if consideration of one or more of the following
46 procedural revisions enables achievement of 70% transport
47 efficiency as follows:
48

Step 1. The flexible tubing between the thermal reactor
system and the bubbler assembly from the experiment
described in Section C.1.2.1 would be
quantitatively rinsed with methanol. This methanol
rinsate would be analyzed for PFOA (as described in
Appendix D.2) and/or for total fluorine (as
described in Appendix D.3). Revised transport
efficiency (TE) as a percentage for PFOA (equation
3) and/or total fluorine (equation 4) would be
computed by including the mass of analyte in the
methanol rinse in the numerator as follows:

$$\% \text{ PFOA TE} = \frac{\text{mass}_{PFOA} \text{ out}}{\text{mass}_{PFOA} \text{ in}} * 100 \qquad (3)$$

where mass_{PFOA} out = mass of PFOA in bubbler
aqueous solution composite
+ mass of PFOA in methanol
rinse

and mass_{PFOA} in = mass of PFOA fed to thermal
reactor system

$$\% \text{ Total F TE} = \frac{\text{mass}_{total\ F} \text{ out}}{\text{mass}_{total\ F} \text{ in}} * 100 \qquad (4)$$

where $\text{mass}_{total\ F}$ out = mass of total F in
bubbler aqueous
solution composite
+ mass of total F in
methanol rinse

and $\text{mass}_{total\ F}$ in = calculated mass of
total F in PFOA fed to
thermal reactor system

Step 2 (if necessary) ~~Reagent(s) would be added to the
bubbler aqueous solution, and the~~ The
experiment described in Section C.1.2.1
would be repeated with reagent(s) (e.g.
NaOH) added to the bubbler aqueous
solution to determine if reagent
addition enhances analyte absorption,
thereby improving transport efficiency.
Transport efficiency would be
calculated using equation (1) and/or
(2) above. The impact of reagent
addition on LOQ for PFOA analysis
described in Appendix ~~B~~D.2 would be

1   determined.
2
3   C.1.3 Reporting of Results
4
5   Following completion of PFOA transport testing as described
6   in this appendix and prior to beginning incineration
7   testing described in Appendix C.2, a brief letter report
8   will be submitted to EPA with the transport efficiency
9   result(s) and indication of what contingent testing, if
10   any, was performed.
11
12   If Appendix C.2 incineration testing is performed, the
13   detailed results of Appendix C.1 transport testing will be
14   included in the final report for Appendix C.2 incineration
15   testing. If Appendix C.2 incineration testing is not
16   performed, the detailed results of Appendix C.1 transport
17   testing will be provided in a test report for Appendix C.1
18   transport testing.

8

1 **APPENDIX D.1**
2 **EXHAUST GAS SAMPLING VIA BUBBLERS**
3
4 Gas samples for off-line analysis will be collected from a
5 vent line off the interface of the thermal reactor system
6 described in Appendix C.2.4. Flexible (silicone or
7 equivalent) tubing will connect the vent line and a set of
8 bubblers.
9
10 Gas absorption via these bubblers will provide aqueous
11 solution (of documented content) to analyze for prescribed
12 parameters. Two to four bubblers (low pressure drop
13 impingers) in series will be used. Each bubbler will
14 contain a predetermined amount of aqueous solution, and the
15 total amount of solution at the beginning of each test run
16 will be a minimum of 55 mL. The temperature of the gas
17 exiting the last bubbler will be monitored.
18
19 An additional empty bubbler (which is empty) will be added |
20 to the front end of this series of bubblers to serve as a
21 knock-out pot if calculations or preliminary measurements
22 indicate that greater than 10 mL of water will be produced
23 during the testing for a given material.
24
25 Upon completion of sample collection, the amount in each
26 bubbler will be weighed and recorded, and the contents of
27 the bubblers will be composited for subsequent analysis.
28 Additionally, the flexible tubing will be rinsed with 5 mL
29 of HPLC water to collect potential condensate in the tubing;
30 this rinsate will be combined with the bubbler composite
31 prior to analysis.
32
33 Bubbler aqueous solution composites will be conveyed to
34 analytical laboratory(ies) in polyethylene, polypropylene,
35 or glass container(s).

9

1 **APPENDIX D.2**
2 **PFOA ANALYSIS BY LC/MS/MS**
3
4 D.2.1 Introduction
5
6 Samples to be analyzed for PFOA in this study will be
7 subjected to Liquid Chromatography with Tandem Mass
8 Spectrometry (LC/MS/MS) in accordance with "Method of
9 Analysis for the Determination of Ammonium
10 Perfluorooctanoate (APFO) in Water Revision 1" (Exygen
11 method) revised per the section-by-section comments listed
12 in Section D.2.4 below. These revisions are necessary to
13 adapt a method originally developed for liter quantity
14 water samples to samples related to testing described in
15 Appendix C.
16
17 The testing programs described in Appendix C are expected
18 to generate samples of aqueous solution, methanol (e.g., as
19 used for extraction or rinsing), and corresponding blanks.
20 The expected sample size for aqueous solution samples (from
21 exhaust gas bubbler sample collection) available for
22 analysis via this method is approximately 50 mL.
23
24 D.2.2 Method Summary
25
26 PFOA is extracted from water using a disposable C_{18} solid |
27 phase extraction (SPE) cartridge. PFOA is eluted from the
28 cartridge with methanol. Quantification of PFOA is
29 accomplished by electrospray liquid chromatography/tandem |
30 mass spectrometry (LC/MS/MS) analysis.
31
32 D.2.3 Reporting
33
34 The target limit of quantitation (LOQ) for this study with
35 this method is 50 ng/L based on prior work with water
36 samples where an 8-fold concentration via extraction using
37 C_{18} SPE cartridge has been demonstrated. The actual LOQ
38 will be matrix dependent; for samples (e.g., methanol
39 rinsate) where the 8-fold concentration cannot be
40 performed, the target LOQ for this study is 400 ng/L.
41
42 Sections 4.5.4 and 5 of the Exygen method explain reporting
43 for field samples such as bubbler aqueous solution |
44 composites, which are distinct from blanks and spikes, such |
45 as the types of samples generated by the testing programs
46 described in Appendix C, as follows: |
47

/0

1   Field samples in which either no peaks or peaks less than the
2   MDL are detected at the corresponding analyte retention time
3   will be reported as ND (not detected). Samples in which
4   peaks are detected at the corresponding analyte retention
5   time that are less than the LOQ and greater than or equal to
6   the MDL will be reported as NQ (not quantifiable).
7
8   Therefore, sample results less than method detection limit
9   (MDL) will be reported as ND, and sample results between
10 MDL and the limit of quantitation (LOQ) will be reported as
11 NQ. Numerical values will not be reported for such
12 samples. Only concentrations above the LOQ, where the
13 reported concentration is attributable to the sample rather
14 than to background, are reported with numerical values.
15
16 Additionally, if the ~~analyte~~ PFOA anion is found in a
17 sample at a concentration above the LOQ for the matrix but
18 is less than 5 times the concentration found in the
19 associated blank, the result will be flagged and treated as
20 ND.
21
22 D.2.4 Study-Specific Comments on the Method
23

Section	Comment
1	• The concentration of PFOA found will be reported directly and the mathematical conversion for reporting as APFO mentioned in the 4th sentence of the 2nd paragraph will not be performed. • Since the 8-fold concentration described in the 2nd sentence 4th paragraph (which forms the basis for the LOQ in the 3rd paragraph and the MDL in the 4th paragraph) is dependent on having a minimum of 40 mL of aqueous sample amenable to extraction using the C_{18} SPE cartridge described in section 4.4 of the method, the LOQ and MDL in the method will be a factor of 8 higher than reported where less than 40 mL of sample is available or where the sample is not amenable to extraction using the C_{18} SPE cartridge described in section 4.4 of the method (e.g., methanol).
3.3 Note at top of page 8	• The note stating "Equivalent materials may be substituted for those specified in this method if they can be shown to produce satisfactory results" will not be used in the analysis for this testing program.

D.2-2

3.3 Notes, Note 1	• The following text will be used in place of Note 1 with respect to the PFOA analysis conducted for this testing program: In order to avoid contamination, the use of disposable labware (tubes, pipets, etc.) is required.
3.3 Notes, Note 4	• The following text will be used in place of Note 4 with respect to the PFOA analysis conducted for this testing program: Solvents (e.g., methanol) used for this analysis must be checked for the presence of contaminants by LC/MS/MS before use.
3.5 opening text prior to 3.5.1	• Where the available amount of sample is expected to be much less than 1 liter, insufficient sample is available to prepare the fortified matrix spikes described in the opening text of section 3.5. In this case, the analytical standards discussed in this opening text will be limited to two purposes since the third purpose (matrix spike) stated in the method cannot be done.
4.3, item b	• Where the available amount of sample is expected to be less than 80 mL (= 2 * 40), the replicate extraction noted in the first sentence of this item cannot be performed. • If the sample is not an aqueous sample amenable to extraction using the C_{18} SPE cartridge described in section 4.4 of the method, then section 4.4 is skipped such that the sample is analyzed directly. (Note: For such samples, the LOQ and MDL will be 8 times higher than the values quoted in the method.)
4.3, item c	• As noted in comment on section 3.5 opening text above, fortified matrix spikes will not be prepared when the available amount of sample is much less than 1 liter. • Where the available amount of sample is expected to be less than 80 mL (= 2 * 40), the conditional repeat fortification and extraction described in the third sentence of this item cannot be performed.
4.4	• Extraction using the C_{18} SPE cartridge requires a suitable aqueous sample. This extraction and the corresponding 8-fold concentration

D.2-3

	pointed out in the NOTE at the end of this section cannot be performed on non-aqueous (e.g., methanol) samples.
4.4, item 1	• In order to measure out the 40 mL mentioned in this item, it is necessary to have at least 45 mL of sample to enable pipet transfer.
4.5.4, item g	• A storage stability study for PFOA in water performed independently of the development of the method indicates that PFOA may be stored in glass, polystyrene, polypropylene, or polyethylene containers without measurable degradation for up to 68 days prior to extraction. Therefore, the total holding time between sample collection and analysis for aqueous PFOA samples in this study may exceed the 14 day limit noted in the first sentence of this item provided that the sample is not held for greater than 68 days unless additional storage stability testing justifies a longer hold time.
4.6, item 3	• As noted in comment on section 3.5 opening text above, fortified matrix spikes will not be prepared when the available amount of sample is much less than 1 liter. In this case, acceptance criteria for matrix spike recoveries will not be considered.
5, item c	• The calculation in equation 3 in this section will not be performed since it is not necessary to convert the PFOA analytical results to APFO for this study.

D.2.5 Reference

Flaherty, J. and K. Risha, "Method of Analysis for the Determination of Ammonium Perfluorooctanoate (APFO) in Water Revision 1", Exygen Method No. 01M-008-046 Revision 1, January 2003. (EPA Docket ID OPPT-2003-0012-0040)

1 **APPENDIX D.3**
2 **WICKBOLD TORCH METHOD FOR TOTAL FLUORINE**
3
4 D.3.1 Introduction
5
6 "The carbon-fluorine bond is exceptionally strong, and
7 extremely vigorous conditions are needed for quantitative"
8 analysis of fluorine in organic compounds. (Kissa, 1998)
9 The "most vigorous" technique for measurement of fluorine
10 in organic compounds is "combustion in an oxyhydrogen
11 flame" referred to as the Wickbold torch. (Kissa, 1998)
12
13 D.3.2 Apparatus
14
15 A typical configuration for the Wickbold oxyhydrogen torch
16 apparatus as described by Sweetser (1956) is shown in
17 Figure D.3-1.
18
19
20 **Figure D.3-1. Wickbold Oxyhydrogen Torch Apparatus**
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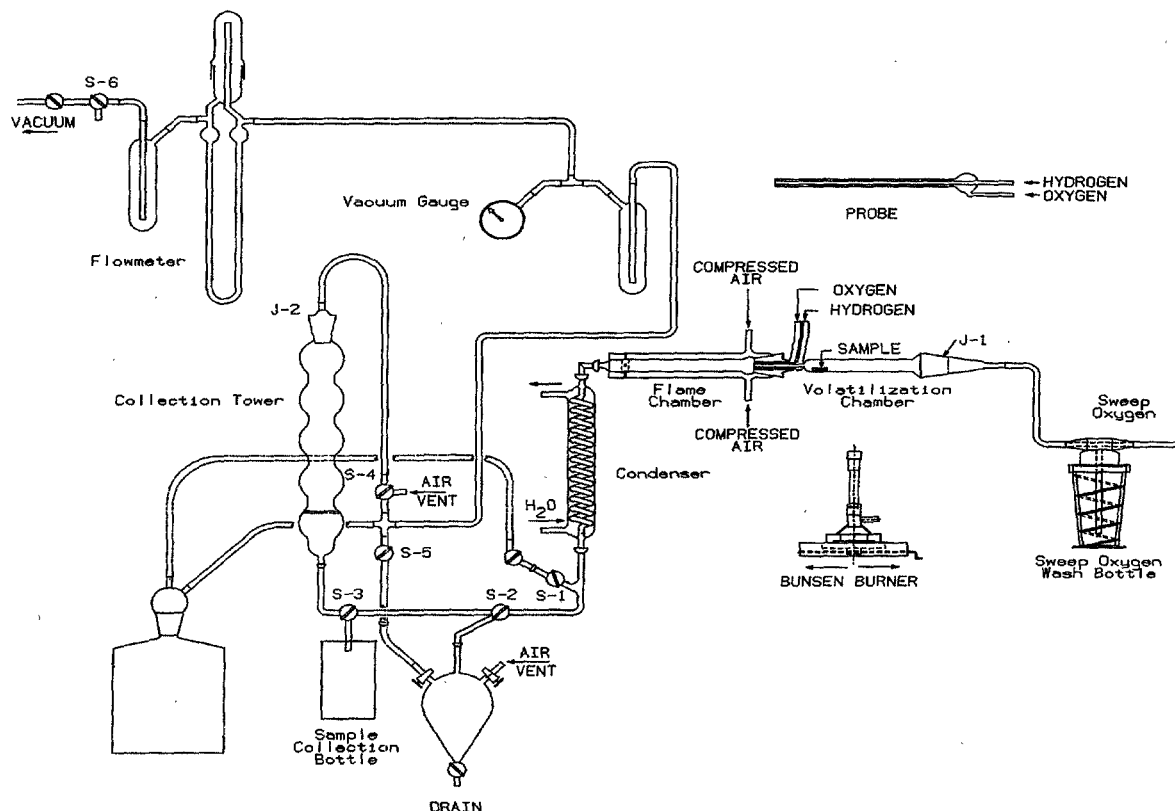
14

1 D.3.3 Method Description
2
3 The sample size for the standard sample boat is up to 20 mg
4 for a solid or up to 5 mL for a liquid.
5
6 With the oxyhydrogen torch in operation, the sample is
7 pyrolyzed or vaporized with a Bunsen burner moving on a
8 rail below the volatilization chamber. The vapors and
9 pyrolysis products are swept through the oxygen-hydrogen
10 flame chamber operating at up to approximately 2000 °C to
11 mineralize the fluorine in the sample to fluoride ion. The
12 resulting fluoride ion is absorbed in the collection tower
13 containing water or an alkaline solution.
14
15 The absorbed fluoride ion is measured via fluoride ion-
16 selective electrode or ion chromatography.
17
18 The reported limit of quantitation for total fluorine via
19 the Wickbold Torch method is 0.5 ppm (0.5 mg/kg). The
20 accuracy of this method for determination of total fluorine
21 in fluorinated polymers is exemplified by total fluorine
22 values of 75.35% to 75.84% for PTFE with known total
23 fluorine content of 76.0%. (Sweetser, 1956)
24
25 D.3.4 Safety Considerations
26
27 Use of hydrogen presents a potential fire and explosion
28 hazard. Use of oxygen presents a potential fire hazard.
29 Safe operation of the oxyhydrogen torch is assured by
30 requires the use of specialized equipment with shielding
31 and elaborate safety devices by well-trained personnel at a
32 qualified laboratory.
33
34 D.3.5 References
35
36 Kissa, E. "Analysis of Anionic Fluorinated Surfactants",
37 Chapter 8 in Anionic Surfactants: Analytical Chemistry –
38 2nd Edition, Revised and Expanded, edited by John Cross.
39 Marcel Dekker Surfactant Science Series, volume 73, 1998.
40
41 Sweetser, P. B. "Decomposition of Organic Fluorine
42 Compounds by Wickbold Oxyhydrogen Flame Combustion Method",
43 Analytical Chemistry, vol. 28, pp. 1766-1768, 1956.

15