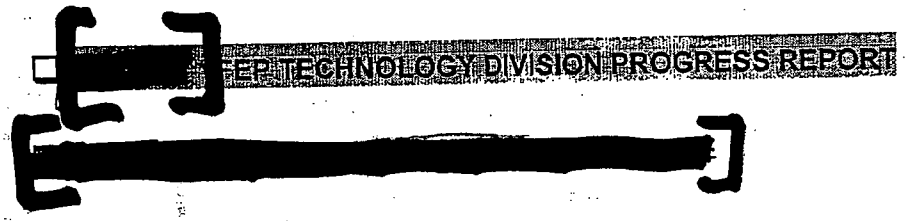
DuPont Fluoroproducts
Washington Works
Melts Technology Report Contribution

Name: Stephen R. Peck *Date: 5/2/03*



TECHNOLOGY REPORT

TABLE OF CONTENTS (ABSTRACT SECTION)

KWIC: [AMMONIUM PERFLUOROOCTANOATE, APFO, C-8, GC, HPLC, Triton® X-100]

Changes to three chromatographic methods for the determination of APFO are described. Included are revisions of gas chromatographic methods for dry resin and air samples and a rapid method for determination of APFO and Triton®X-100 in aqueous samples by liquid chromatography.

(STEPHEN R. PECK)

TEFLON®
TECHNOLOGY REPORT
ARTICLES SECTION

I. SAFETY, HEALTH AND ENVIRONMENTAL

B. *ANALYTICAL DEVELOPMENTS FOR DETERMINATION OF AMMONIUM PERFLUOROOCTANOATE*

STEPHEN R. PECK, S. Hopkins, M. Jacobs, S. Mayle, M. A. Parsons, M. E. Reeder, D. Riggs

Summary

Changes to three chromatographic methods for the determination of APFO are described. Included are revisions of gas chromatographic methods for dry resin and air samples and a rapid method for determination of APFO and Triton®X-100 in aqueous samples by liquid chromatography.

This report describes recent analytical method developments intended to enhance the effectiveness of the determination of APFO content of various sample types. Changes to three procedures will be discussed separately. A reference to this report will be included in the method procedures to document the technical basis for the changes.

Part I: Determination of APFO in dry resin by gas chromatography:

This method is performed in the [redacted] control lab as WW-3690. In this procedure, the dry sample is treated with acidic methanol to convert the APFO to its methyl ester. The ester is extracted into hexane and analyzed by GC-ECD. An internal standard is included, and the response of its ester is used to normalize the peak for the methyl-PFO.

Originally, WW-3690 was used almost exclusively for PTFE fine powder resins, but the application of the procedure has been broadened to dry FEP and PFA fluff, [redacted] fluoroadditive, process filters, and other dry material.

WW-3690 requires a significant amount of sample preparation and handling compared to other GC methods in [redacted] Lab. One complication was the use of a spinning riffler to yield a "representative" sample of resin. In order to obtain a single analytical result, 4 tests had to be performed:

1. Sample blank
2. APFO external calibration sample
3. Polymer "control" (standard) sample
4. Process sample

The original method specified use of 1.000 ± .001 grams of C-8 solution – extremely difficult to achieve for a methanol solution. Nonadecafluorodecanoic acid (C-10) was used as an internal standard. A "blank" (containing C-10) was tested to account for residual APFO in the C-10 solution. Adjusting the APFO response for each sample to compensate for this impurity led to a complex series of calculations.

The internal standard was originally used to account for differences in injection volume. With the acquisition of auto-injectors, variation in injection volume is small; however, an internal standard is still needed for this test. It is observed that the internal standard peaks are depressed in the presence of polymer. This is possibly due to interaction of the fluorinated (C-x) esters with the polymer surface, and a portion of the ester is not available for injection on the GC. The internal standard is used to adjust the sample response for incomplete recovery of the esters. The APFO peak is divided by the internal standard peak to yield a normalized response factor.

The following components of the method were examined for possible simplification of the procedure as a way to improve cycle time and avoid introduction of error due to unnecessary steps:

1. Discontinuing use of spinning riffler.
2. Discontinue the "blank" sample.
3. Replace C-10 with less toxic perfluoroheptanoic acid (C-7).
4. Revise calculations to incorporate actual mass of APFO used as an external standard.
5. Replace the polymer control sample with statistical monitoring of the response of the APFO external calibration solution.

To compare the impact of these changes, a sample of [redacted] was tested by the method procedure (Procedure 1) and the revised procedure (Procedure 2). Four replicates were tested. Results are in Table SRP-1:

Table SRP-1: APFO content (ppm)

	Procedure 1	Procedure 2
	0.9	1.9
	0.6	1.1
	0.9	1.5
	1.1	1.1
average	0.9	1.4

Procedure 2 shows slightly higher results; however, this difference is considered acceptable for two reasons. First, the specification limit for residual APFO in [redacted] is 15 ppm. Second, all of these results approach the quoted sensitivity of 1 ppm for the method. Due to advantages of faster cycle time, less toxic internal standard, and streamlined calculations, the changes have been incorporated into WW-3690. To replace the polymer control sample, a response factor for the external calibration solution as follows:

Factor = [(C8 peak/ C7 peak)/ mass used].

Part II: Determination of APFO in air samples:

This procedure (WW-3627) has been used for several years for industrial hygiene monitoring of personnel exposure. A portable pump is used to draw a known volume of air through a specially-treated Tenax® trap. The Tenax® is then flushed into a vial, and the eluted APFO is determined by GC-ECD. Historically, C-10 has been used as an internal standard, and the tubes were individually treated with a mixture of reagents in [redacted]

One objective of this study was to evaluate eliminating the use of the internal standard. Since all samples are tested as clear solutions, there are no surface interactions to affect recovery of the C-8 ester (see above). Since an auto-injector is used, and a series of external standards are run with each series of air samples, use of an internal standard is redundant.

A second objective of this test was to compare a batch of tubes that were commercially treated by SKC to those prepared in B-3.

The treated Tenax tubes were "spiked" with weighed amounts of a standard APFO solution (1.0 microgram/mL). A series of external standards were used as outlined in WW-3627. The GC response of each tube was then used to calculate an observed APFO loading. This was divided by the calculated loading to calculate the recovery efficiency for each tube. Results are in Tables SRP-2 through 5. The average recovery for each set exceeds 100%.

One factor is possibly the accuracy of the digital pipet used to deliver aliquots of standard APFO solutions for the calibration plots.

Calibration plots prepared with C-10 internal standard (old procedure) and with no internal standard are shown in Figures SRP-1 and 2, respectively. Linearity is comparable and slightly better w/o C-10. Recoveries averaged 113% for the C-10 method vs. 111% with no internal standard. The results indicate that the internal standard is not needed. Comparable results were also noted between Tenax® traps which had been prepared in B-3 vs. using traps that were pretreated by SKC. For the B-3 traps, average recovery was 113%. The SKC traps showed an average recovery of 110%. Based on these results, it is recommended that the use of the internal standard be discontinued and that the pre-treated Tenax® traps may be used for WW-3627.

Table SRP-2: APFO Recovery (%); C-10 Internal Standard

tube	ug added	ug found	%recovery
10--6	0.2469	0.2751	111
10--9	0.2021	0.2293	113
10--12	0.1790	0.2034	114
10--21	0.2829	0.3194	113
10--24	0.1863	0.2025	109
10--27	0.1563	0.1841	118
10--30	0.1209	0.1371	113

average % recovery: 113

Table SRP-3: APFO Recovery (%); No Internal Standard

tube	ug added	ug found	%recovery
0-4	0.3016	0.34010	113
0-7	0.3527	0.38485	109
0-10	0.4630	0.43338	94
0-13	0.1583	0.19637	124
0-15	0.1405	0.17720	126
0-19	0.2913	0.2979	102
0-22	0.2053	0.2063	100
0-25	0.1440	0.1601	111
0-28	0.0930	0.1075	116

average % recovery: 111

Figure SRP-1: Calibration Plot (C-10 Internal Standard)

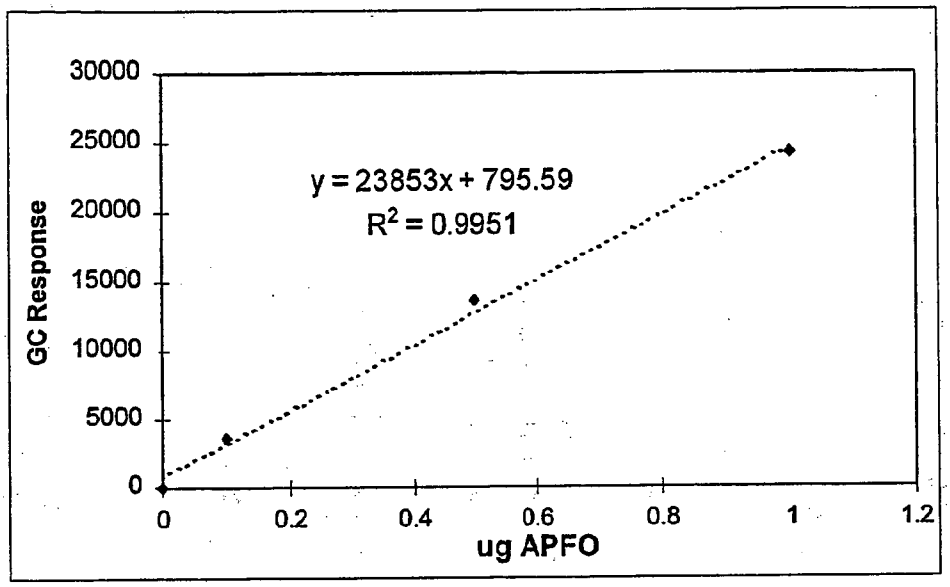


Figure SRP-2: Calibration Plot (No Internal Standard)

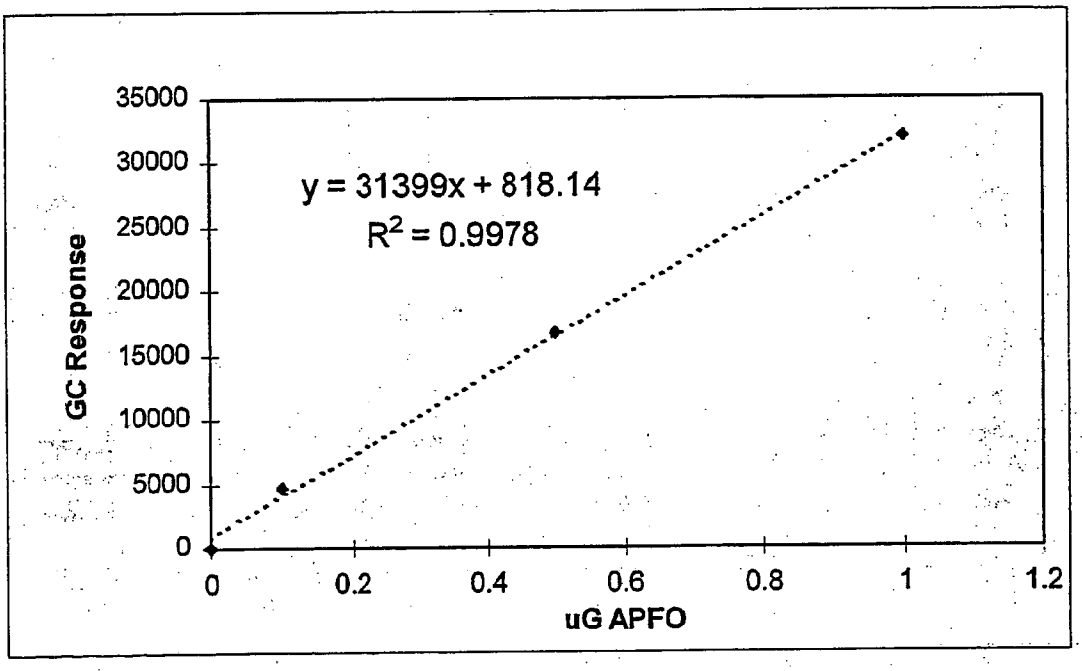


Table SRP-4: APFO Recovery (%); Tenax® Prepared in B-3

tube	ug added	ug found	%recovery
10–6	0.2469	0.2751	111
10–9	0.2021	0.2293	113
10–12	0.1790	0.2034	114
0-4	0.3016	0.34010	113
0-7	0.3527	0.38485	109
0-10	0.4630	0.43338	94
0-13	0.1583	0.19637	124
0-15	0.1405	0.17720	126

average % recovery: 113

Table SRP-5: APFO Recovery (%); Tenax® Prepared by SKC

tube	ug added	ug found	%recovery
10–21	0.2829	0.3194	113
10–24	0.1863	0.2025	109
10–27	0.1563	0.1841	118
10–30	0.1209	0.1371	113
0-19	0.2913	0.2979	102
0-22	0.2053	0.2063	100
0-25	0.1440	0.1601	111
0-28	0.0930	0.1075	116

average % recovery: 110

Part III: Determination of APFO and Triton® X-100 in aqueous media:

In 2002, the determination of APFO in aqueous media at Washington Works was significantly improved by the acquisition of an Agilent HPLC (Reference 1). The method requires minimal sample preparation and a 10-minute analysis time.

We have begun receiving supernate and other aqueous samples for the simultaneous determination of APFO and Triton® X-100. Both compounds give a UV response and can be analyzed by HPLC; however, the retention time for Triton is nearly 1 hour on our standard method (see Figure SRP-3). Altering the composition of the mobile phase led to a significantly shorter analysis time (see Figure SRP-4). A detailed comparison of the two HPLC methods is given in Table SRP-6. A 2 micron filter is used to remove polymer solids from the samples prior to injection.

Figure SRP-3:

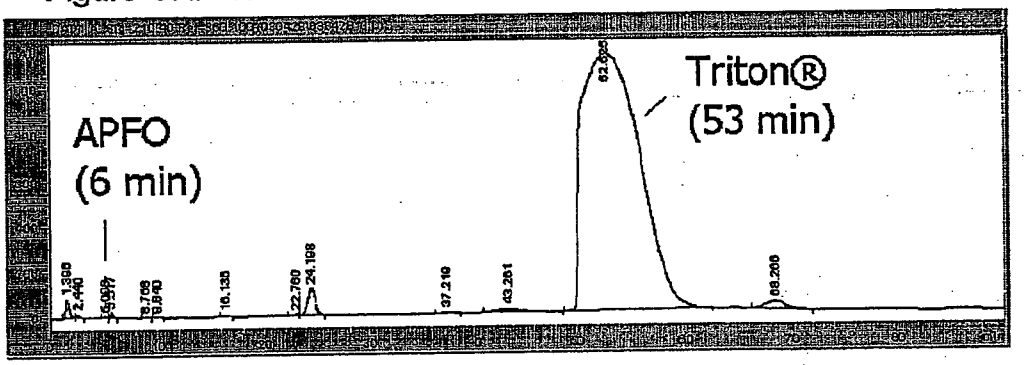
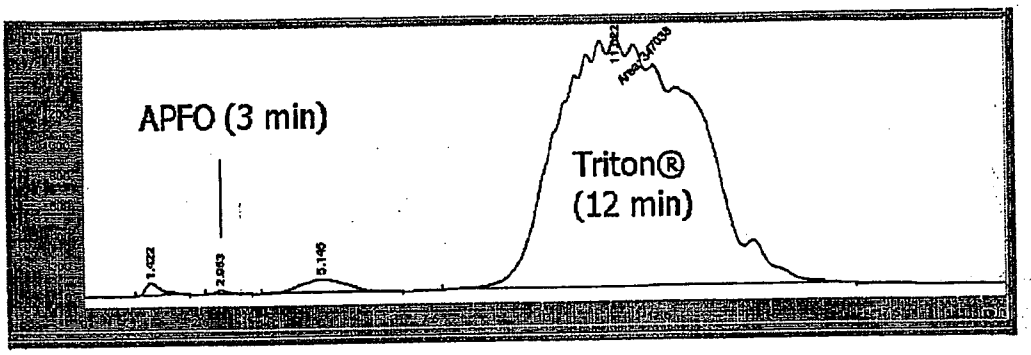


Table SRP-6: HPLC Method Comparison

	Mobile Phase Composition (% of flow)		run time	~ Retention Time (minutes)	
Perchloric Acid (0.6%)	Acetonitrile	Water	(min)	APFO	Triton
10	40	50	90	6	53
10	50	40	20	3	12

Figure SRP-4:



Reference 1: [redacted]

FEP Dispersion

Product	Lot #	Meas APFO ppm Wet Basis
		982
		1013
		1020
		1145
		5351
		5649
		5942
		5341
		6201
		6227
		1762
		1335
		1733
		1733

PFA Dispersion

Product	Lot #	Meas APFO ppm Wet Basis
		2302
		3462
		3350
		3442
		3466
		1925

PTFE Dispersion

Product	Lot #	Meas APFO ppm Wet Basis
		565
		575
		625
		448
		492
		1052
		1126
		928
		1268
		922
		536
		565
		626
		480
		504
		545
		540
		522
		486
		445
		533
		638
		568

RMS 137 Resin	C8 (ppm)
	0.4
	3.0
	0.5
	1.0
	1.4
	0.9
	1.3
	1.3
	1.0
	1.1
	1.2
	1.2
	1.0
	1.0
	1.0
	1.0
	1.0
	1.0
	1.1
	1.4
	1.0
	1.0
	2.0
	1.0
	2.0
	5.0
	1.0
	1.0

RMS 137 Resin	C8 (ppm)
	0.7
	0.1
	1.3
	1.1
	1.0
	1.5
	1.0
	1.9
	1.1
	1.0
	2.0
	1.0
	2.5
	1.5
	1.4
	1.4
	1.0
	0.9
	0.8
	1.2
	0.8
	1.2
	4.7
	1.1
	2.0
	0.7
	1.7
	1.0
	0.5
	1.6
	0.5
	1.5
	0.5