TNO Triskelion

Utrechtseweg 48
P.O. Box 844
3700 AV Zeist
The Netherlands

www.triskelion.nll

T +31 88 866 28 00
F +31 88 866 69 70

TNO Triskelion Report

V20318

Residual content of F-Diox Acid Ammonium Salt and its thermal decomposition products in a PTFE film

Date	12 April 2013
Authors	[redacted]
Sponsor	Solvay Specialty Polymers Italy S.p.A.
TNO Triskelion project number	093.20444/01
TNO Triskelion study code	-
Sponsor's study code	-
Status	Final
Previous versions	-
Number of pages	44
Number of tables	2
Number of figures	19
Number of annexes	3
Number of appendices	-

Abbreviations

EU	European Union
EFSA	European Food Safety Authority
FIA – ESI	Flow Injection Analysis with electro spray ionization mass detection
GC-MS	Gas Chromatography with Mass detection
LC-MS	Liquid Chromatography with Mass detection
UPLC	Ultra Performance Liquid Chromatography
MRM	Multi Reaction Monitoring
PTFE	Polytetrafluoroethylene

Annex 3 Determination of the residual content of F-Diox Acid Ammonium Salt in a PTFE film

Contents

1 Introduction

Acetic acid, 2,2-difluoro-2-[[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy]-,ammonium salt (1:1) or F-Diox Acid Ammonium Salt (CAS Nr 1190931-27-1) is intended to be used as an emulsifier/dispersing agent in the polymerisation process of fluorinated polymers (PTFE). After manufacture, residual F-Diox Acid Ammonium Salt may remain in the final food contact material, and subsequently migrate into foodstuffs. The analytical method described below, allows for the determination of the residual content of F-Diox Acid Ammonium Salt in a PTFE film.

2 Scope

This method describes an analytical procedure for the determination of the residual content of F-Diox Acid Ammonium Salt in a PTFE film in an approximate analyte concentration of 4 – 400 ng/ml. The final range expressed in mg per 6 dm² or mg/kg polymer will depend on the concentration step, if any, applied prior to analysis for the level of F-Diox Acid Ammonium Salt and on the surface/weight ratio of the polymer investigated in the study.

3 Principle

The sample is extracted with an appropriate solvent by refluxing for 4 hours. After the extraction period, the level of F-Diox Acid Ammonium Salt extracted from the sample is determined using liquid chromatography with mass detection (LC-MS). Quantification is performed by means of an external standard calibration.

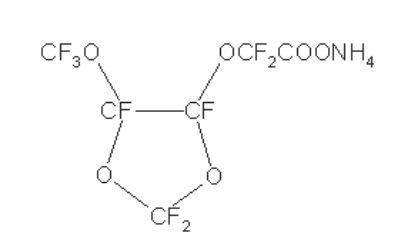
4 Reagents

NOTE: *Reagents shall be of analytical quality*.

4.1 Analyte

4.1.1. Chemical name: Acetic acid, 2,2-difluoro-2-[[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy]-,ammonium salt (1:1) - 41.9% solution in water

Synonym: F-Diox Acid Ammonium Salt
Trade name: Cyclic C6O4 Ammonium Salt
CAS number: 1190931-27-1
Molecular weight: 357.08
Molecular formulae: C6H4O6NF9
Structure:



4.2 Chemicals and Reagents

4.2.1 Acetone, AR Biosolve

4.2.2 HFE7100 or 3M™Novec™ Engineered Fluid HFE-7100
Composition : HFE-7100 fluid ($C_4F_9OCH_3$) consist of two inseparable isomers with essentially identical properties. These are $(CF_3)CFCF_2OCH_3$ (CAS No. 16702-08-7) and $CF_3CF_2CF_2$-CF_2OCH_3 (CAS No. 163702-07-6)
Supplier : 3M™ Novec™
Boiling point : 56°C, HFE7100 is known to swell PTFE polymer

4.2.3 Methanol : (Biosolve Cat no. 13680501 Lot no. 804911)

4.2.4 Ammoniumacetate: (p.a. Merck)

4.2.4 Water : MilliQ

4.3 Solutions

4.3.1 Stock solution of F-Diox Acid Ammonium Salt (4.19 mg/ml)

Transfer 100 µl of the F-Diox Acid Ammonium Salt solution in a 10 ml volumetric flask and fill to the mark with water. Mix carefully.

4.3.2 Diluted stock solution of F-Diox Acid Ammonium Salt (41.9 µg/ml)

Transfer 100 µl of the stock solution (4.3.1) in a 10 ml volumetric flask. Fill the flask to the mark with water and mix carefully.

4.3.3 Calibration solutions of F-Diox Acid Ammonium Salt (4 – 400 ng/ml)

From the diluted stock solution (4.3.2), prepare calibration solutions containing 0.2, 0.4, 1.0, 2.0, 5.0 and 10 µg of F-Diox Acid Ammonium Salt per ml water.

Into a series of 10 ml volumetric flasks, transfer 1, 2, 5, 10 25, 50, 75 and 100 µl of the diluted stocksolution of F-Diox Acid Ammonium Salt (4.3.2) and fill the volumetric flasks the mark with water. Mix the solutions thoroughly. The calibration solutions contain 4.19, 8.38, 20.95, 41.9, 104.75, 209.5, 314.25 and 419.0 ng F-Diox Acid Ammonium Salt/ml water. Fill the calibration solutions in LC vials.

5 Apparatus

NOTE: *An instrument or item of apparatus is listed only where it is special or made to a particular specification; usual laboratory glassware and equipment being assumed available.*

5.1 **LC-MS system** whose main components include a liquid chromatographic system preferably with an automatic injector and a mass spectrometer (MS) detector operating in negative mode

The following chromatographic conditions have been found suitable:

LC apparatus:
Orbitrap LTQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an Ion Max ESI source, an Accela pump, an Accela autosampler and an Accela Photo Diode Array Detector.

Flow injection ESI negative mode:

Column:	No column, only 1 m(L) x 0.25 mm (I.D) PEEK tubing as restriction
Eluent:	50% Methanol + 0.1% NH_4OH in MilliQ water
Injection volume:	2 µl
Flow:	250 µl/min
Scan range:	125-1250
Monitoring ion:	m/z 338.95

6 Sample preparation

6.1 Test sample preparation

Establish the weight and the area of the test sample. Cut the test sample into small pieces, put it in an 200 ml erlenmeyer flask and reflux for 4 hours in 100 ml of a mixture of HFE7100/acetone (80/20). After 4 hours reflux, cool the solution down to room temperature. Take 1 ml of the extract, evaporate gently under a nitrogen stream to dryness and redissolve the residue 1 ml water. Fill a LC vial with the solution thus obtained.

Treat blank extraction solvent, i.e. without polymer test sample, throughout the whole procedure.

6.2 Recovery experiments

Add a known amount of F-Diox Acid Ammonium Salt to 100 ml of a mixture of HFE7100/acetone (80/20), reflux for 4 hours. After 4 hours reflux, proceed as described for the test sample preparation as described in 6.1.

7 Procedure

7.1 Analysis

NOTE: *When starting measurements, baseline stability and response linearity of the detector should be examined, together with verification of the detection limit. The same operating conditions of the LC-MS system shall be maintained through out the analysis of all test samples and solutions set out in section 6. Each test sample shall be analysed at least in triplicate.*

7.2 Sample treatment

Test sample extracts, blanks, recovery samples, as well as calibration solutions are analysed by LC-MS.

7.2.1 Calibration solutions

Inject each of the calibration solutions (4.3.3) into the LC system, using the conditions given in Section 5. Measure the peak area of the analyte in the chromatograms obtained and plot the area against the concentration of the analyte in the calibration samples in ng analyte per ml.

NOTES: Two sets of calibration solutions made from independently prepared stock solutions should be cross-checked and should agree to ± 5 % of one another on the basis of peak ratio measurement.

7.2.2 Test samples and recovery solutions

Inject each of the solutions obtained according to section 6.1 and 6.2 into the LC system, using the conditions given in Section 5. Measure the peak area of the analyte in the chromatogram obtained.

7.3 Quantification

7.3.1 *Calculation of the analyte concentration in the test samples*

Graphical determination:

Using the peak area values obtained from the test samples according to 7.2.2, read the analyte concentration in the extracts from the calibration graph (7.2.1) in ng/ml.

Calculation from the regression parameters:

Use the measured peak area as obtained in 7.2.2 in the following formula.

If the regression line equation is linear

y [peak area] = a * x [ng/ml] + b,

with:
y = detector response
a = regression coefficient
b = intercept
x = concentration of the analyte

then the analyte concentration in the solution C is

$C_{sol} = (y-b)/a$

Both procedures yield directly the analyte concentration in the sample extracts in ng/ml

NOTE: The method applying calculation from the regression parameters should be the preferred one.

7.3.2 Calculation of the residual content

Calculate the residual content (QMA) of the analyte per 6 dm^2 from the test sample as follows:

$QMA\ (mg/6\ dm^2) = (C_{sol} \times V \times 6)/(A \times 10^6)$

In which:

C_{sol} (ng/ml) = concentration of the analyte in the tests sample extract injected for LC analysis;
A (dm^2) = area of test sample extracted
V = 100 ml (volume of extraction solvent)

Calculate the residual content (QM) of the analyte per kg polymer from the test sample as follows:

$QM\ (mg/kg) = (C_{sol} \times V)/(W \times 10^3)$

In which:

C_{sol} (ng/ml) = concentration of the analyte in the tests sample extract injected for LC analysis;
V = 100 ml (volume of extraction solvent
W (g) = weight of test sample extracted

8 Detection limit and precision

8.1 Detection limit

The detection limit is based on the lowest calibration solution of 4 ng/ml. The signal to noise ratio for a solution containing 4 ng analyte/ml is higher than 3:1.

8.2 Recovery and repeatability

The mean recovery and standard deviation were calculated from the recovery experiments with blank extraction solvent which was spiked with F-Diox Acid Ammonium Salt and subsequently refluxed for 4 hours (6.2). The recovery of F-Diox Acid Ammonium Salt at a spike level of 41.9 µg/100 ml extract, after reflux for 4 hours in HFE7100/Acetone was found to be 124 ± 5%.

8.3 Calibration curve

The calibration curve should be linear. The correlation coefficient should be equal to or higher than 0.996.

9 Test report

The test report shall contain, as a minimum, the following:

- an identification
- name of the laboratory
- name of the person responsible for the analysis
- date of the report
- date of the analysis
- chemical name of the analyte
- a reference to the method of analysis
- the performance characteristics of the method
- sample details, such as:
    * type of food/food simulant/material/article
    * date of receipt of the sample, its origin and its denotation
    * date of preparation of the laboratory sample
    * conditions of storage of sample and laboratory sample
- results expressed in mg analyte per 6 dm^2.
- results should be reported as the average value from two or more determinations.
- reasons for modification of the method of analysis, if applied