



Determination of Kerojet 8118 content in Aviation Turbine Fuel using High Performance Liquid Chromatography followed by Low-Resolution Tandem Mass Spectrometry

0 Introduction

This standard describes a method for determining the concentration of Static Dissipater Additive (SDA) Kerojet 8118 in Aviation Turbine Fuel (ATF).

For determination of other SDAs in ATF please additionally refer to ASTM D7524 / IP 568. A combination of both methods must be applied where a mixture of Kerojet 8118 and other SDAs may be present.

1 Scope

This standard describes a method for the determination of the SDA Kerojet 8118 in ATF in the range of 0.5 mg/l to 5 mg/l.

WARNING – The use of this method may involve hazardous materials, operations and equipment. This standard does not purport to address all of these safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Normative References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3170, *Petroleum liquids - Manual sampling*

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling*

EN ISO 4259 Part 1, *Petroleum and related products – Precision of measurement methods and results – Part 1: Determination of precision data in relation to methods of test*

3 Principle

The concentration of Kerojet 8118 in ATF samples is determined by a standard addition method using High Performance Liquid Chromatography (HPLC) coupled to Low Resolution tandem Mass Spectrometry (LRMS). Electrospray ionization (ESI) or heated electrospray ionization (HESI) is used to protonate the analytes. Multiple Reaction Monitoring (MRM) is used to detect Kerojet 8118 in ATF.

Oligomer molecules only specific for Kerojet 8118 are selected as analytes. To perform the MRM, the protonated oligomer molecule with the elemental composition $C_{67}H_{128}N_2O_2$ (monoisotopic mass = 992.9976 Da) and its major homologous with variations in aliphatic chain length ($\pm C_2H_4$) and degree of unsaturation ($\pm H_2$) are used as precursor ions. Their corresponding fragment ions result in the neutral loss of the alkyl amine chains. The intensities of all MRM transitions listed in Table 2 are summed to enhance the signal intensity for quantification.

The quantification is carried out by the addition of appropriate concentrations of the Kerojet 8118 reference solution directly to the ATF sample.



4 Reagents and Materials

- 4.1 **Ammonia solution 25% v/v**, analytical grade
- 4.2 **Methanol (MeOH)**, LCMS grade
- 4.3 **Tetrahydrofuran (THF)**, LCMS grade
- 4.4 **2-Propanol (IPA)**, LCMS grade
- 4.5 **Kerojet 8118¹**, reference solution 100%
- 4.6 **Blank Aviation Turbine Fuel (ATF) not containing Kerojet 8118**

5 Apparatus

For detailed experimental conditions and parameters please refer to Annex A.

- 5.1 **HPLC system:** High Performance Liquid Chromatography (HPLC) system comprising of an autosampler, quaternary HPLC pump and column compartment.
- 5.2 **MS system:** Triple quadrupole mass spectrometer.
- 5.3 **Analytical balance:** capable of weighing to 0.1 mg precision.
- 5.4 **25 ml volumetric flask, Grade A.**
- 5.5 **10 ml volumetric flask, Grade A.**
- 5.6 **Dropping pipette.**
- 5.7 **Positive displacement autopipettes** capable of delivering 1 to 10 µl, 10 to 100 µl, 50 to 250 µl and 100 to 1000 µl.
- 5.8 **LC Autosampler vials (1.5 ml)**, with crimp cap or screw cap with poly-isobutene septa.

6 Sampling

- 6.1 Take a sample of at least 200 ml in accordance with EN ISO 3170 or EN ISO 3171 or in accordance with the requirements of national standards or regulations for the sampling of petroleum products.
- 6.2 Use dedicated ATF sampling equipment.
- 6.3 Use amber glass or epoxy-lined metal containers with inert closures.

7 Preparation of quality controls and spiked ATF samples

Use of clean laboratory equipment, measuring flasks and positive displacement pipettes is essential due to the low level of detection necessary. All solutions shall be freshly prepared and used within two days.

7.1 Preparation of stock solution

Prepare two independent stock solutions. Place a 25 ml glass volumetric flask (5.4) onto the balance (5.3) and tare. Use a dropping pipette (5.6) and add 250 +/- 1.0 mg of Kerojet 8118 reference solution (4.5). Fill up to the mark with THF to give a 10.000 mg/l stock solution 1. Repeat this procedure with another 25 ml glass volumetric flask to produce stock solution 2.

7.2 Preparation of working solution

The stock solutions of 7.1 are further diluted. Take a calibrated adjustable autopipette (5.7) and transfer 200 µl of stock solution 1 into a 10 ml glass volumetric flask (5.5) and 200 µl of stock solution 2 into another 10 ml glass volumetric flask (5.5) and fill both up to the mark with THF to get working solution 1 and working solution 2. Each working solution contains 200 mg/l. Use working solution 1 to prepare the quality controls and working solution 2 to spike the ATF samples.

¹ For information about the availability of Kerojet 8118 please contact the EI.



7.3 Preparation of quality controls and spiked ATF samples

7.3.1 Preparation of quality control samples

To prepare Quality Control samples (QC) of 0.5 and 3 mg/l Kerojet 8118 in ATF (4.6) pipette 25 and 150 µl (using a calibrated adjustable autopipette) of working solution 1 (WS1, see 7.2) into separate 10 ml glass volumetric flask (5.5) and fill both up to the mark with ATF (4.6). Shake well and transfer 1 ml each into LC autosampler vials (5.8) using dropping pipettes (5.6), add cap and crimp.

7.3.2 Preparation of spiked ATF samples

To spike the ATF samples for quantification, take an adjustable autopipette (5.7) and transfer 25, 50 100 and 150 µl of working solution 2 (WS2, see 7.2) into separate 10 ml glass volumetric flasks (5.5) and fill each to the mark with the ATF sample to be quantified (see Table 1). Shake well and transfer 1 ml of each solution into LC autosampler vials (5.8) using dropping pipettes (5.6), add cap and crimp. As unspiked reference, transfer 1 ml of the pure ATF sample to be quantified into a LC autosampler vial.

Table 1: Volumetric dilution for spiking the ATF sample with 0.5, 1, 2 and 3 mg/l of Kerojet 8118

Kerojet 8118 (mg/l) Spiked	Volume WS2 (µl)	ATF Sample (ml)
0.5	25	10
1.0	50	10
2.0	100	10
3.0	150	10

8 Apparatus preparation

8.1 MS parameter

The compound specific parameter for the MRM transitions and the source parameter for the ionization (see Annex A) may have to be optimised for specific instruments. Some of these parameters may also be named differently. In this case follow the instructions for the MRM optimisation from the manufacturer.

The column dimensions shall be used as described in Annex A with the flow rate of 2 ml/min and an eluent split of 1 to 10 to the MS.

8.2 HPLC parameter

Stainless steel tubing is recommended to connect the HPLC modules and MS as THF may lead to swelling of Polyetheretherketone (PEEK) tubing and may give rise of higher blanks.

8.3 HPLC/MS

The HPLC/MS shall be tuned, purged and equilibrated according to the manufacturer's recommendation.

9 Procedure

9.1 Prepare all the samples as described in clause 7. A fixed amount of each sample, which may be between 20 – 40 µl to give the best instrument response, is injected into the HPLC system (sample set order, see 9.4).

9.2 Prepare Eluent A and B (see Annex A) in adequate amounts, place them in the HPLC system and purge the HPLC pump.

9.3 Equilibrate the HPLC/MS system.

9.4 Start your sample set (9.1) with 2 Blanks (ATF 4.6) followed by the QC samples (7.3.1). Now run the ATF test sample set (7.3.2) in the order Blank, pure ATF test sample and spiked ATF test samples. Between every ATF test sample set measure a Blank. After 3 ATF test sample sets measure a Blank, the QC samples and another Blank. An example of a sample set table is given in Annex D.

10 Peak identification and integration

All the MRM transition listed in Table 2 are summed to one signal to enhance the signal intensity compare to the single MRM transitions.

The retention time of the peak is typically 1.1 min +/- 0.3 min. The peak is integrated using the features of the dedicated software package to give values of peak area and height. If the retention time is outside these limits, check the instrument.



Table 2: List of MRM transitions specific for Kerojet 8118

Precursor ions (<i>m/z</i>)	Fragment ions (<i>m/z</i>)
966.0	698.7
968.0	726.7
968.0	700.7
968.0	698.7
994.0	726.7
996.0	754.7
996.0	728.7
996.0	726.7
1022.0	754.7
1024.1	782.8
1024.1	756.8
1024.1	754.7

NOTE: regarding experience from method development only the peak of Kerojet 8118 is monitored with these MRM transitions.

11 Calculation

Calculating the amount of Kerojet 8118 in the ATF test sample using the standard addition method

Establish a calibration curve of peak area vs. Kerojet 8118 concentration spiked to the ATF test sample set. The area of the pure ATF test sample is correlated to 0 concentration spiked. Use linear regression to obtain the best fit to the recorded data.

The equation of the linear calibration curve consists of:

$$A = a + b \cdot C_{(\text{Kerojet 8118})}$$

A chromatographic peak area [counts·s]

a, b regression coefficients

$C_{(\text{Kerojet 8118})}$ amount of Kerojet 8118 in [mg/l]

The parameters “a” and “b” are determined by linear regression with equal weighting of the data.

The amount of Kerojet 8118 $C_{(\text{Kerojet 8118})}$ in the ATF test sample is obtained by the following equation:

$$C_{(\text{Kerojet 8118})} = (A - a) / b$$

The amount of Kerojet 8118 $C_{(\text{Kerojet 8118})}$ in the ATF test sample is obtained at the point if $A = 0$:

$$C_{(\text{Kerojet 8118})} = | - a / b |$$

The absolute value is reported as concentration.

12 Expression of results

12.1 Report the Kerojet 8118 content as:
 $C_{(\text{Kerojet 8118})}$ in mg/l, rounded to the nearest 0.1 mg/l.

12.2 For results below 0.5 mg/l, report as:
 $C_{(\text{Kerojet 8118})} < 0.5$ mg/l.

13 Precision

The precision of this method has not yet been established.

14 Test report

The test report has to include at least the following information:

- a reference to this standard;
- the type and complete identification of the product tested;
- the results of the test (see clause 12);
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.



Annex A

(normative)

HPLC:	Column:	C18 modified silica material without polar embedded groups, in this study XBridge BEH C18 (3.5 μ m, 20 x 4.6 mm) was used <ul style="list-style-type: none">➤ XBridge BEH C18 columns can be used over the entire range of mobile phase pH (1-12)➤ Methanol with 1% ammonia solution was used to extract the oligomer molecules directly from jet fuel➤ Under 1% ammonia all amines are unprotonated and undergo only hydrophobic interactions with the stationary phase, their hydrophobic character is increased, and they can be adsorbed on the C18 column in presence of 99% methanol																								
	Injection volume:	20 μ l of ATF samples																								
	Column temperature:	50°C																								
	Flow rate:	2.0 ml/min																								
	Eluent:	A: MeOH containing 1 % of the ammonia solution 25 % B: THF																								
	Total run time:	4 min																								
	Gradient:	<table border="1"><thead><tr><th>t /min</th><th>0</th><th>0.6</th><th>0.8</th><th>2.0</th><th>3.0</th><th>3.2</th><th>4.0</th></tr></thead><tbody><tr><td>A /%</td><td>100</td><td>100</td><td>60</td><td>1</td><td>1</td><td>100</td><td>100</td></tr><tr><td>B /%</td><td>0</td><td>0</td><td>40</td><td>99</td><td>99</td><td>0</td><td>0</td></tr></tbody></table>	t /min	0	0.6	0.8	2.0	3.0	3.2	4.0	A /%	100	100	60	1	1	100	100	B /%	0	0	40	99	99	0	0
t /min	0	0.6	0.8	2.0	3.0	3.2	4.0																			
A /%	100	100	60	1	1	100	100																			
B /%	0	0	40	99	99	0	0																			
	Needle-flushing solution:	2-Propanol																								
	Eluent split to MS:	1 to 10 via PEEK-SIL																								



consolidated version from 16. July 2019

MS: Ionization: Electrospray ionization (ESI) or heated electrospray ionization (HESI) can be used
Polarity: Positive ion mode
Resolution Q1, Q3: 0.7 +/- 0.1 Da FWHH (full width at half height)

Source Parameter (need to be optimised regarding the instrument used):

Curtain Gas (CUR):	20
Collision Gas (CAD):	Medium
Ion Spray Voltage (IS):	5500
Temperature (TEM):	500
Ion Source Gas (GS1):	40
Ion Source Gas (GS2):	80

Compound Parameter (need to be optimised regarding the instrument used):

Declustering Potential (DP):	30
Entrance Potential (EP):	10
Collision Energy (CE):	75
Collision Cell Exit Potential (CXP):	35

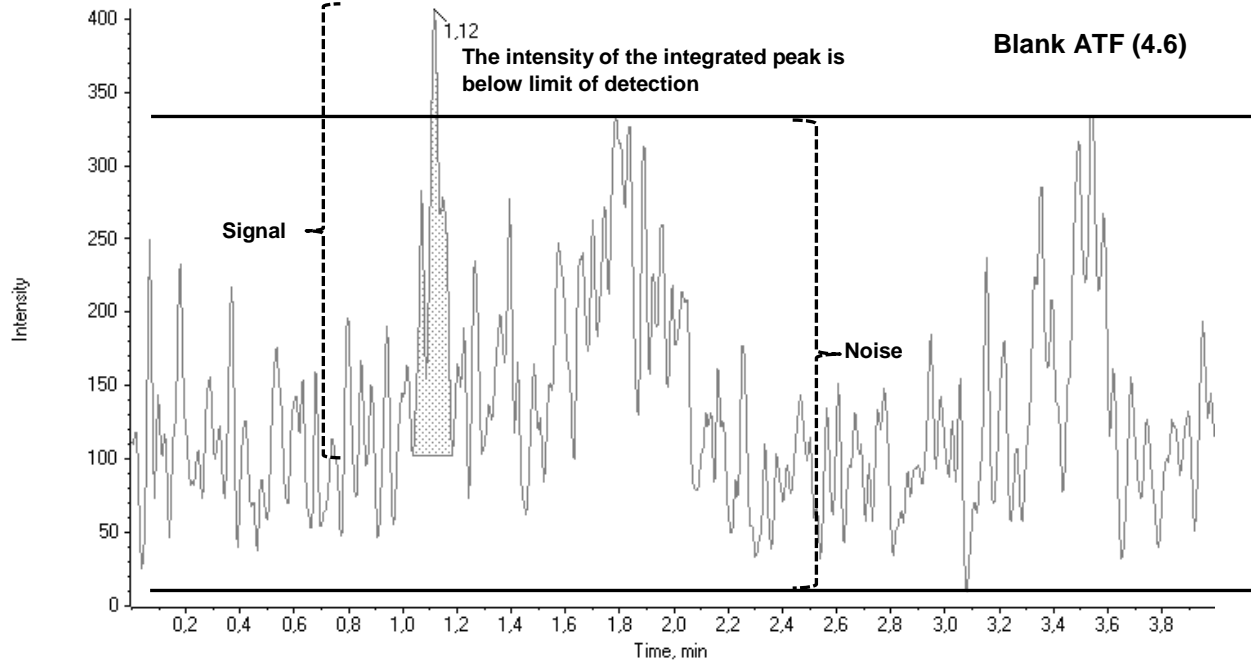


Annex B

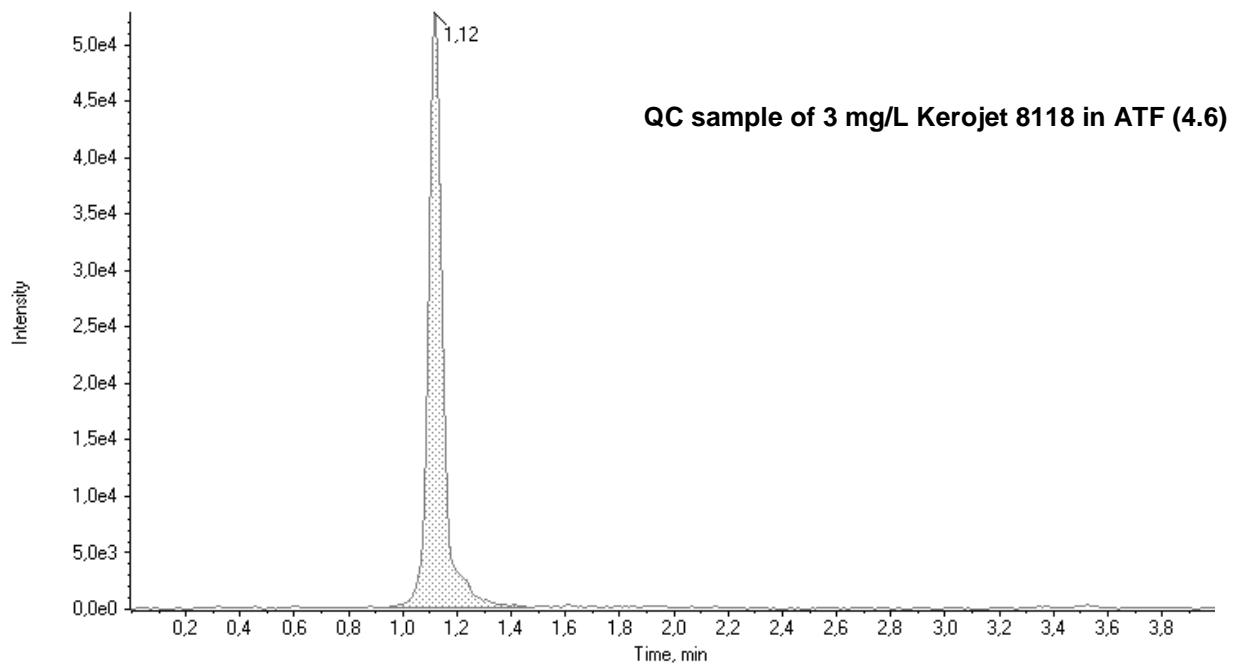
(informative)

B.1 Chromatograms

Blind Flugbenzin (Jet-A1) - Kerojet 8118 (Unknown) 966,0 / 698,7, 968,0 / 726,7, 968,0 / 700,7, 968,0 / 698,7, 994,0 / 726,7, 996,0 / 754,7, 996,0 / ...
Area: 1,201e3, Height: 3,040e2, RT: 1,12 min



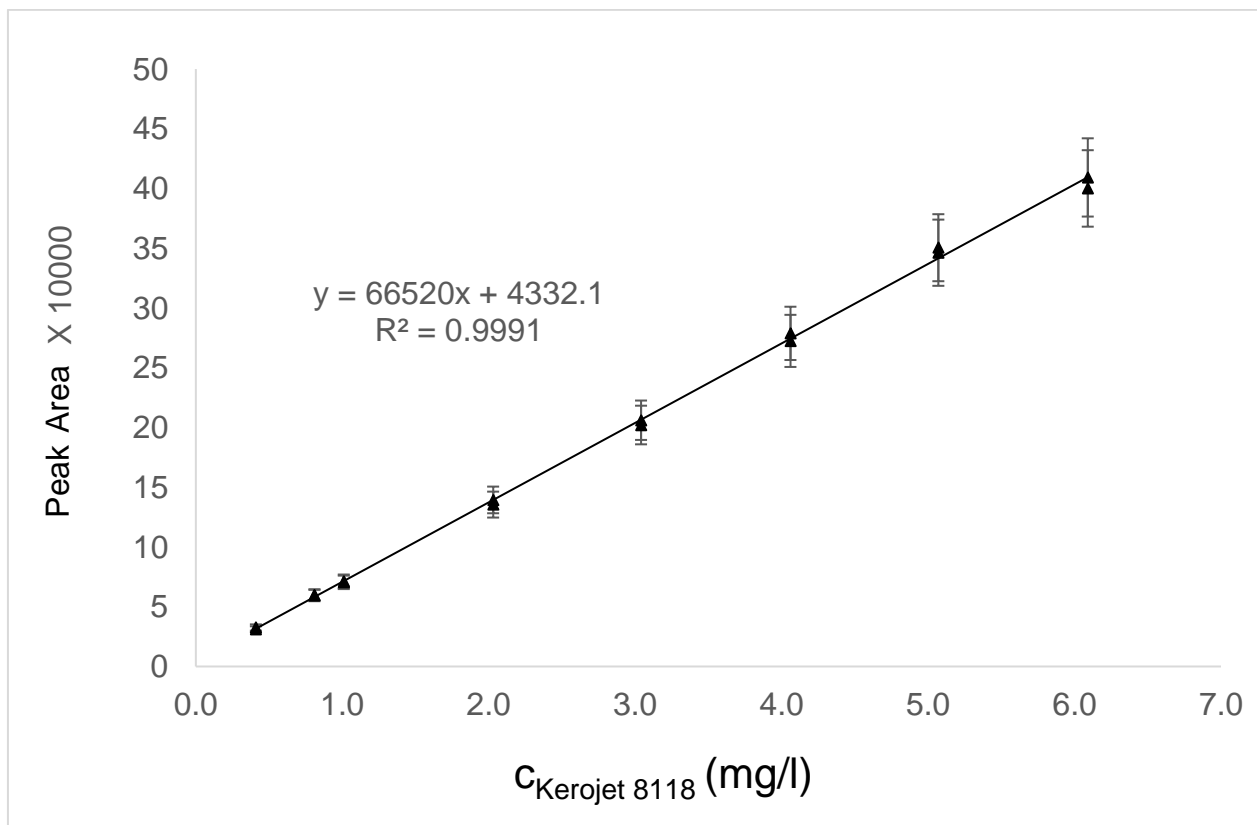
Kerojet 8118 in Jet A1 (Innospec_K7_180725_1 - Kerojet 8118 (Quality Control) 966,0 / 698,7, 968,0 / 726,7, 968,0 / 700,7, 968,0 / 698,7, 994,0 / ...
Area: 2,005e5, Height: 5,274e4, RT: 1,12 min



B.2 Calibration curve

Table 3: Volumetric Dilution for preparing calibration standards in the range of 0.2 to 7 mg/l Kerojet 8118 in ATF blank matrix

Kerojet 8118 (mg/l)	Volume WS1 (µl)	Volumetric Flask (ml)	Filling Solvent
7.0	350	10	ATF
6.0	300	10	ATF
5.0	250	10	ATF
4.0	200	10	ATF
3.0	150	10	ATF
2.0	100	10	ATF
1.0	50	10	ATF
0.8	40	10	ATF
0.4	20	10	ATF
0.2	10	10	ATF



Example of a calibration curve (0.4 to 6 mg/l) received during method development.



B.3 Recoveries

amount of Kerojet 8118 spiked [mg/l]	amount of Kerojet 8118 determined [mg/l]	recovery /%
1.1	1.1	97
2.1	2.1	99
4.2	4.4	104

Recoveries received during method development:

Annex C

(informative)

Specificity of the method – Jet A1 containing Innospec’s Stadis® 450 (Figure C.1) and Jet A1 containing Afton’s Hitec® 4547 (Figure C.2) showed a clearly resolved peak of identical height and area when spiked with 3 mg/l Kerojet 8118.

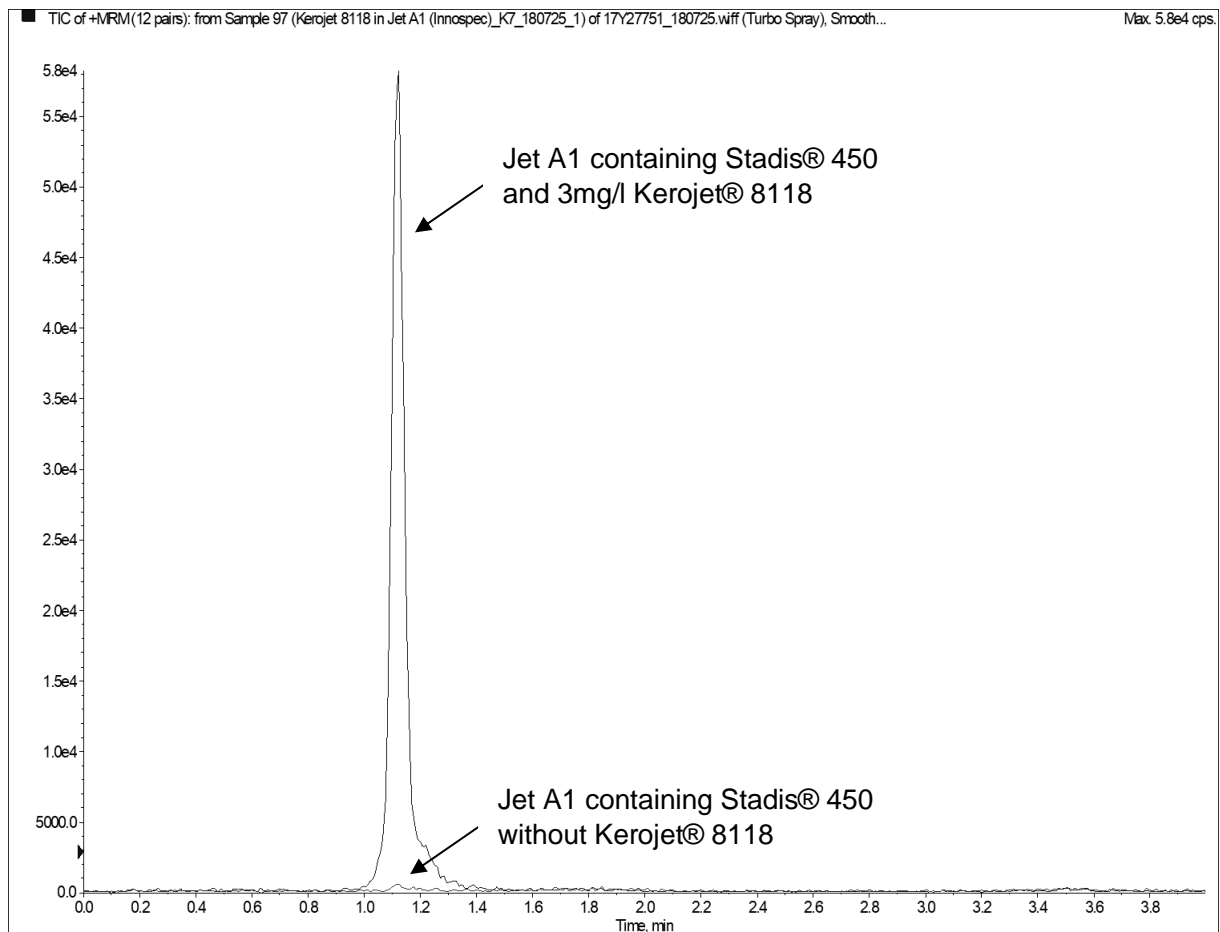


Figure C.1: Jet A1 containing Stadis® 450 spiked with 3 mg/l Kerojet 8118 versus Jet A1 containing Stadis® 450 alone.

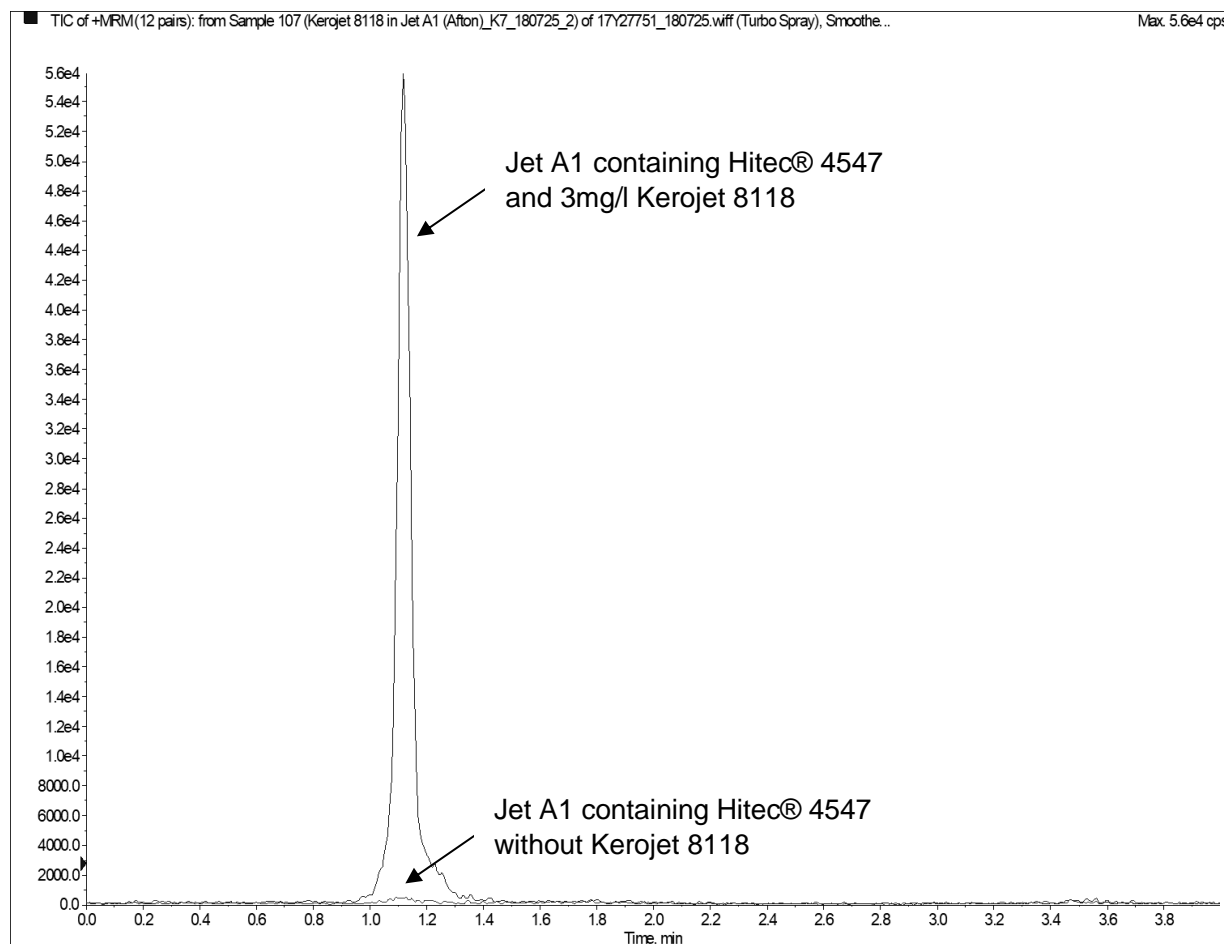


Figure C.2: Jet A1 containing Hitec® 4547 spiked with 3 mg/l Kerojet 8118 versus Jet A1 containing Hitec® 4547 alone.



Annex D

(informative)

D.1 Example table for one sample set (refer to 9.4)

selected injection volume: 20µl

no. of run	sample	comment
1	Blank	ATF without Kerojet 8118 (see 4.6)
2	Blank	ATF without Kerojet 8118 (see 4.6)
3	QC sample 0,5 mg/l	LOQ (limit of quantification)
4	QC sample 3.0 mg/l	expected range
5	Blank	ATF without Kerojet 8118 (see 4.6)
6	ATF test sample	
7	ATF test sample spiked with 0.5 Kerojet 8118	
8	ATF test sample spiked with 1.0 Kerojet 8118	
9	ATF test sample spiked with 2.0 Kerojet 8118	
10	ATF test sample spiked with 3.0 Kerojet 8118	
11	Blank	ATF without Kerojet 8118 (see 4.6)
12	QC sample 0.5 mg/l	LOQ (limit of quantification)
13	QC sample 3.0 mg/l	expected range
14	Blank	ATF without Kerojet 8118 (see 4.6)