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TNO Report

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Characterization of migrating oligomers and reaction products of Fluorolink 7800:7850 from a fluoropolymer sample

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Summary

At the request of Solvay Solexis, a study was performed to characterize the migrating oligomers and reaction products of Fluorolink 7800:7850 from a fluoropolymer sample. Fluorolink 7800:7850 is used as an emulsifier/dispersing agent during the polymerisation process of fluoropolymers.

A sample of fluoropolymer produced by using 0.2% of Fluorolink 7800:7850 was extracted with 95% ethanol for 6 hr at 60°C. The migration extract was analysed using GC-MS and LC-MS for the presence of any reaction product(s) and/or oligomer(s) of Fluorolink 7800:7850.

For the GC analysis MS data were collected in the scan mode [redacted].
For the LC, samples were directly injected (flow injection) in the system. [redacted].

Standard solutions of Fluorolink 7800:7850 in 95% ethanol were injected for reference purposes.

In order to exclude the loss of any volatile component, the migration extract was analyzed in two ways: 1) directly, without any concentration step and 2) after concentration of the migration extract to a small volume.

GC-MS analysis [redacted] did not show any signal for the standard solutions in 95% ethanol, containing Fluorolink 7800:7850 at a level of 10 µg/ml and 50 µg/ml. No differences were found in the GC chromatograms of the standard solutions containing Fluorolink 7800:7850 (10 µg/ml and 50 µg/ml), blank 95% ethanol and the sample extracts which were injected directly, i.e. without the concentration step. For the concentrated sample extract, the GC chromatogram showed an increased noise level and an increased signal for the peaks already detected in the blank extracts. No additional peaks were found in the GC chromatograms of the sample extracts.

[redacted] Fluorolink 7800:7850 at a level of 10 µg/ml and 50 µg/ml.
Not any signal corresponding to the Fluorolink standard solutions was found in the 95% ethanol sample extracts obtained after 6 hr 60°C.

The detection limit of the LC-MS method applied is considered to be equal to the standard solution containing Fluorolink 7800:7850 at a level of 10 µg/ml.
Taking a surface to volume ratio of 3.38 dm²/ 100 ml [redacted] of Fluorolink 7800:7850 [redacted] is considered to be not detectable, i.e. less than 9 µg/6 dm² or less than 9 µg/kg food.

Contents

1 Introduction

Solvay Solexis has requested to perform a migration study on Fluorolink 7800:7850, in order to obtain information on the identification and quantification of migrating reaction products(s) and/or oligomer(s) of Fluorolink 7800:7850. Fluorolink 7800:7850 is used as an emulsifier/dispersing agent during the polymerisation process of fluoropolymers.

In an initial study, the residual content of Fluorolink 7800:7850 in a final fluoropolymer was found <20 µg/kg resulting in a worst case migration of < 1 µg per kg foodstuff, while overall migration into 95% ethanol after 6 hr at 60°C was found 0.48 mg/6 dm² (TNO report V7054, October 2006).
In the determination of the residual content it was found that no oligomers of Fluorolink 7800:7850 with [redacted] were present in the fluoropolymer sample tested (after extraction with a mixture of methanol/water), while ^{1}H-NMR of the 95% ethanol migration extract showed the absence of any other reaction product or oligomer of Fluorolink 7800:7850.

In order to obtain additional information on the identification and quantification of migrating reaction products(s) or oligomer(s) of Fluorolink 7800:7850, including migration of any volatile substances, the migration study was repeated in 95% ethanol (6 hr at 60°). The migration extract was analysed for the presence of any Fluorolink 7800:7850 reaction product(s) and/or oligomer(s) using GC-MS and LC-MS.

2 Procedure

The sample material was brought into contact with 95% ethanol for 6 hr at 60°C. In order to obtain data for any migrating volatile and non-volatiles substances, aliquots of the extract were directly analysed by the use of gas chromatography in combination with mass spectrometry (GC-MS) and Liquid Chromatography (direct flow injection) in combination with mass spectrometry; the remaining of the extract was concentrated to a small volume followed by analysis using GC-MS and LC-MS.
Standard solution of Fluorolink 7800:7850 in 95% ethanol was injected on both GC and LC for reference purposes.

2.1 Sample materials

Solvay Solexis, Bollate (Mi) Italy, provided sample material for testing. The sample was provided with a unique TNO sample code. The sample was received in March 2008 and stored at room temperature. In addition, a sample of the reference substance Fluorolink 7800:7850 was received.

Table 1: Samples used for the study

TNO sample ID	Solvay Solexis sample ID	remark
[redacted]	Fluorolink 7850	Used for reference
[redacted]	Fluoropolymer [redacted] [redacted]	Sheets 13 x13 cm Thickness ca. 0.04 cm

[redacted] = propane, 1,1,1,2,2,3,3-heptafluoro-3-[(trifluoroethenyl)oxy]-, polymer with tetrafluoroethene and trifluoro(trifluoromethoxy)ethane, produced by using 0.2% of Fluorolink 7800:7850. The sample tested was manufactured according the same process of the samples tested previously (TNO report V7054, October 2006) and hence the polymerization recipe is a 40% aqueous dispersion in which the content of the surfactant is about 0.2% w/w of the full recipe; this content is equivalent to 0.5% w/w of the solid content. Based on the above considerations, the level of surfactant in the samples tested in this study is 0.5% w/w of the dry matter.

Fluorolink 7800 and 7850 are mixtures of perfluoro-acids with the following simplified notation:

species	n	m	Molecular weight
N1	0	0	296,5
N2	1	0	462,5
M3	1	1	578,5
N3	2	0	628,5
M4	2	1	744,5
N4	3	0	794,5
N5	4	0	960,5

Where n and m are the coefficients of the general formula:
C_3F_6ClO-$[CF_2$-$CF(CF_3)$-$O]_n$-$[CF(CF_3)$-$O]_m$-CF_2COOH

Where n ranges from 1 to 4 and m from 0 to 2 in the active species.

In this test report the substance name is indicated as Fluorolink 7800:7850, while actually Fluorolink 7850 was tested. Fluorolink 7800 is a "sub-set" of Fluorolink 7850.
Both products are covered by the same CAS. No. 329238-24-6; the differences are in Molecular Weight (lower in 7800) and Molecular Weight Distribution (wider in 7850).
Therefore Fluorolink 7850 should be considered the "worst-case".

2.2 Determination of the migration of reaction product(s) and/or oligomer(s) of Fluorolink 7800:7850

Per test, two sheets of fluoropolymer (one sheet is 13 cm x 13 cm, i.e. 1.69 dm² per sheet or 3.38 dm² for two sheets, taking one side into account) were cut into pieces of ca. 2x2 cm and transferred into a 250 ml Scott flask. An amount of 100 ml 95% ethanol (preheated at 60°C) was added to the polymer sample. The flask was closed with a gas-tight cap and placed in an oven for 6 hours at 60°C. After this period, the migration solution was cooled down and an aliquot of 0.5 ml of the 95% migration solution was injected directly for GC-MS and LC-MS analysis.

The remaining migration solution was evaporated to dryness at 60°C under a nitrogen stream, redissolved in 0.5 ml 95% ethanol and injected for GC and LC-MS analysis.

Blank values were obtained by treatment of 100 ml of 95% ethanol in the same way as described above (without adding fluoropolymer).

All experiments were carried out in triplicate.

Typical chromatograms obtained for the determination of the migration of reaction products(s) and/or oligomer(s) of Fluorolink 7800:7850 from the fluoropolymer samples into 95% ethanol are presented in Figures 3–12 and 15-18.

2.3 Standard solutions of Fluorolink 7800:7850

For reference purposes, standard solutions of Fluorolink 7800:7850 were prepared in 95% ethanol at a level of 10 µg/ml and 50 µg/ml

The standard solutions were analysed by GC/MS and LC-MS as described below in item 3.
Typical LC-MS chromatograms and GC/MS chromatograms obtained for the standard solutions are in Figures 1, 2, 13 and 14.

3 Characterization of the migration solution

Blank 95% ethanol and migration solutions in 95% ethanol were injected directly for analysis and after concentration of the migration solution, as described in 2.1. Standard solutions of Fluorolink 7800:7850 (see 2.3) were injected for reference and semi-quantification purposes.

GC-MS conditions
Column : Alltech AT 5ms ; 30 m x 0.25 mm; film thickness 0.25 µm
Injector: 250°C; splitless;
Injection volume: 1 µl
Carrier gas: Helium, 1.8 ml/min.
Oven: Initial temperature 80°C for 2 minutes → 20°C/minute
Final temperature 325 °C for 10 minutes

The temperature of the MS transfer line was 325 °C. MS data were collected in the scan mode (m/z 15-800).

LC-MS conditions:
Blank, migration and standard solutions were analysed by Ion Trap- Mass Spectrometry (LC-IT-MS) in the ESI(+) and in the ESI (-) mode.
10 µl of the solutions were directly injected (flow injection) in the system, using MeOH: ammonium acetate (5 mM) 1:1 (v/v) at a flow rate 300 µl/min. [redacted].

4 Results and discussion

LC-MS analysis

[redacted]Fluorolink 7800:7850[redacted].

[redacted] Fluorolink 7800:7850 [redacted] Fluorolink 7800:7850[redacted] [redacted].

In the sample extracts (both directly analysed and concentrated prior to analysis, Fig. 4 and 6) no additional peaks were obtained compared to the spectra of blank 95% ethanol (Fig. 3 and 5).
Not any signal corresponding to the Fluorolink standard solutions was found in the 95% ethanol sample extracts obtained after 6 hr 60°C.

In the ESI [redacted] mode the spectra obtained for the standard solutions (Fig. 7 and 8) show some additional peaks for Fluorolink 7800:7850 when compared to the blank solutions (Fig. 9 and 11). However, the signals in the ESI [redacted] mode are less evident then in the ESI [redacted] mode

The detection limit of the LC-MS method applied is set at 10 µg/ml (standard solution containing Fluorolink 7800:7850 at a level of 10 µg/ml).
Taking a surface to volume ratio of 3.38 dm²/ 100 ml [redacted] Fluorolink 7800:7850 [redacted] is considered not detectable, i.e. less than 9 µg/6 dm² or less than 9 µg/kg food.

GC-MS analysis ([redacted])
No differences were found in the GC chromatograms of the standard solutions containing Fluorolink 7800:7850 (10 µg/ml and 50 µg/ml), blank 95% ethanol and the sample extracts which were injected directly, see Figures 13-16.

For the concentrated sample extract, the GC chromatogram (Figure 18) showed an increased noise level and an increased signal for the peaks already detected in the blank extracts (Figure 17).
No additional peaks were found in the GC chromatograms of the sample extracts.

5 Signatures

We, the undersigned, hereby declare that this report constitutes a true and accurate record of the procedures employed and of the results obtained in this study.

[redacted] Date:

[redacted] Date:

[redacted] Date:

6 Appendix A

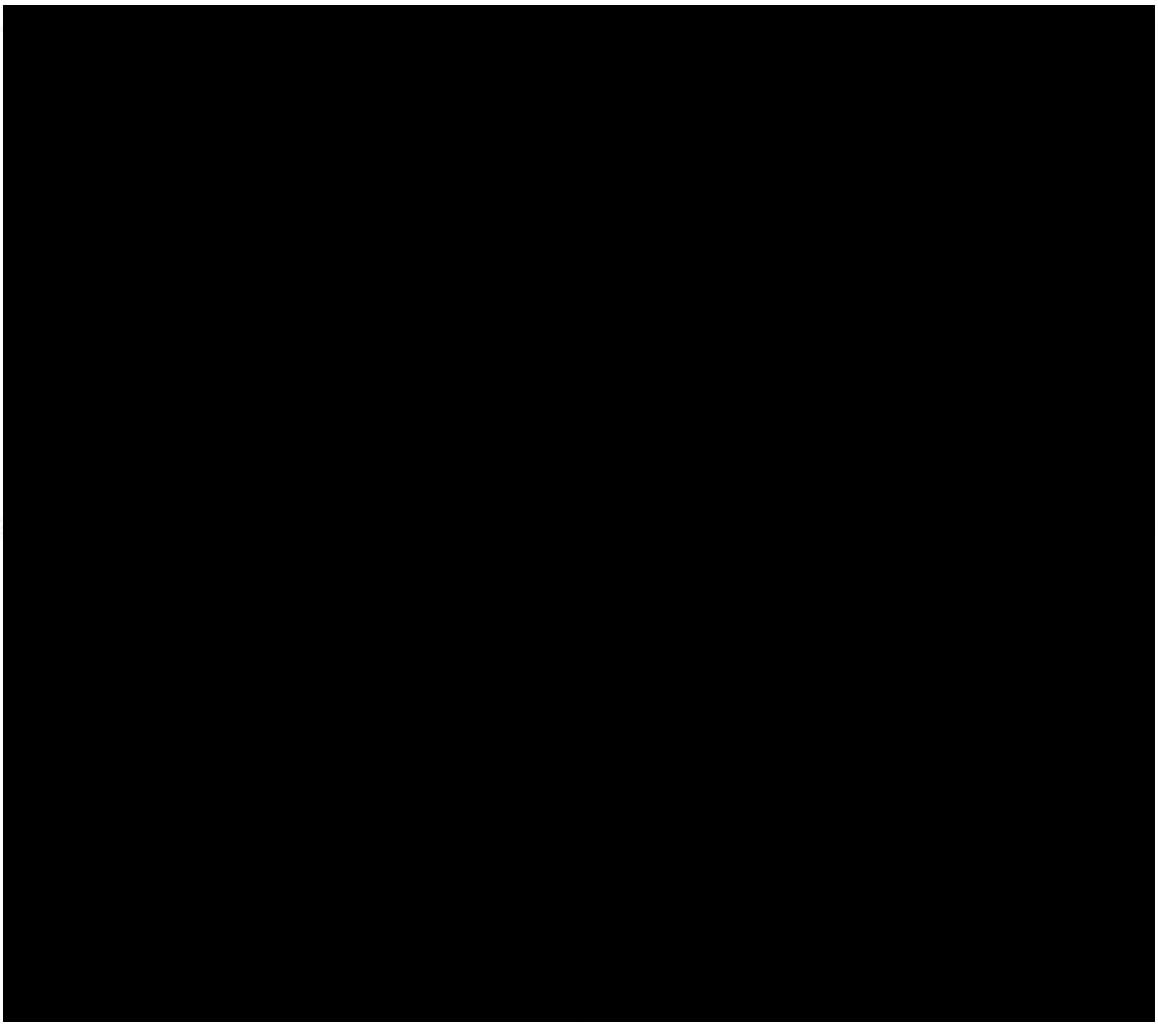

Fig 1 - LC-MS analysis – [redacted]

Standard solution Fluorolink 7800:7850 in 95% ethanol – 10 µg/ml

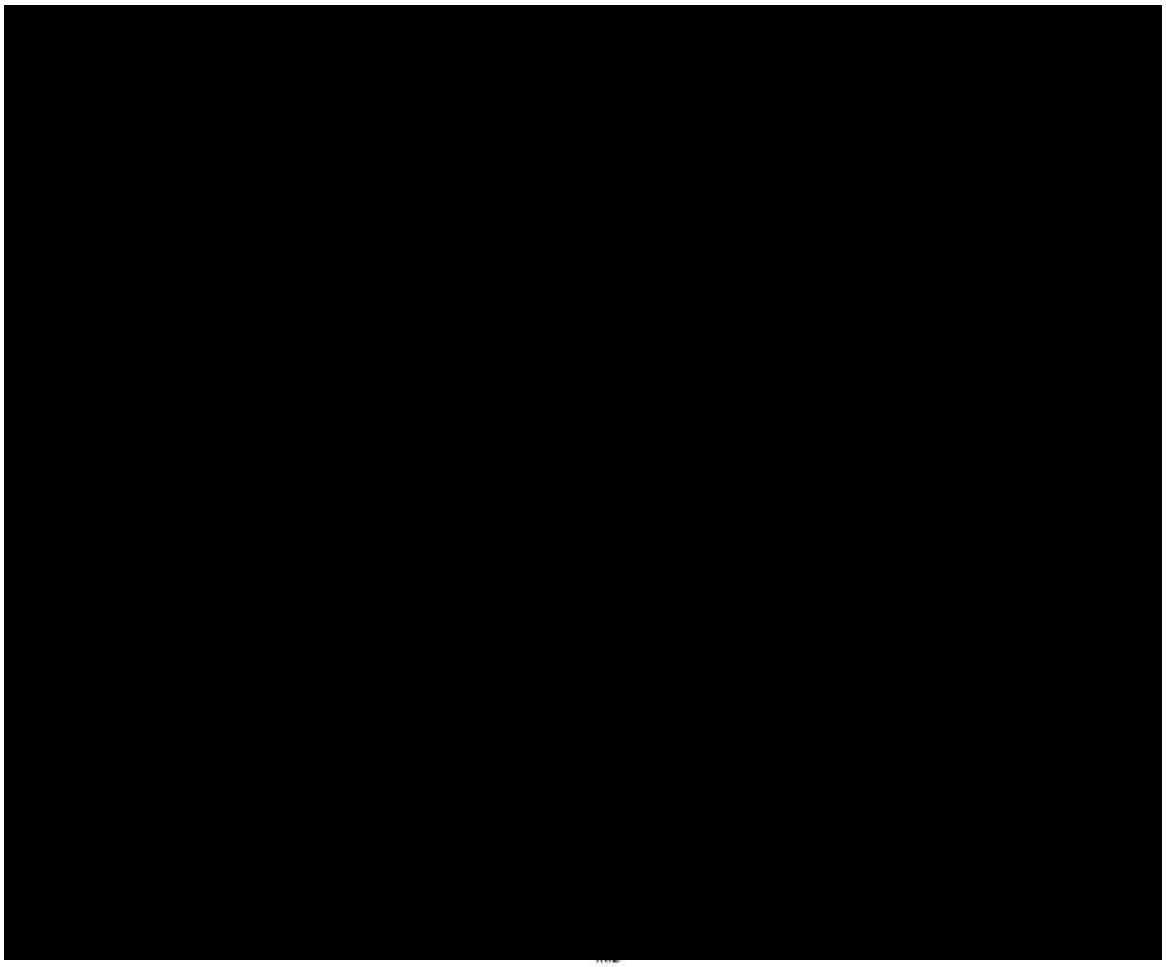

Fig 2 - LC-MS analysis – [redacted]

Standard solution Fluorolink 7800:7850 in 95% ethanol – 50 µg/ml

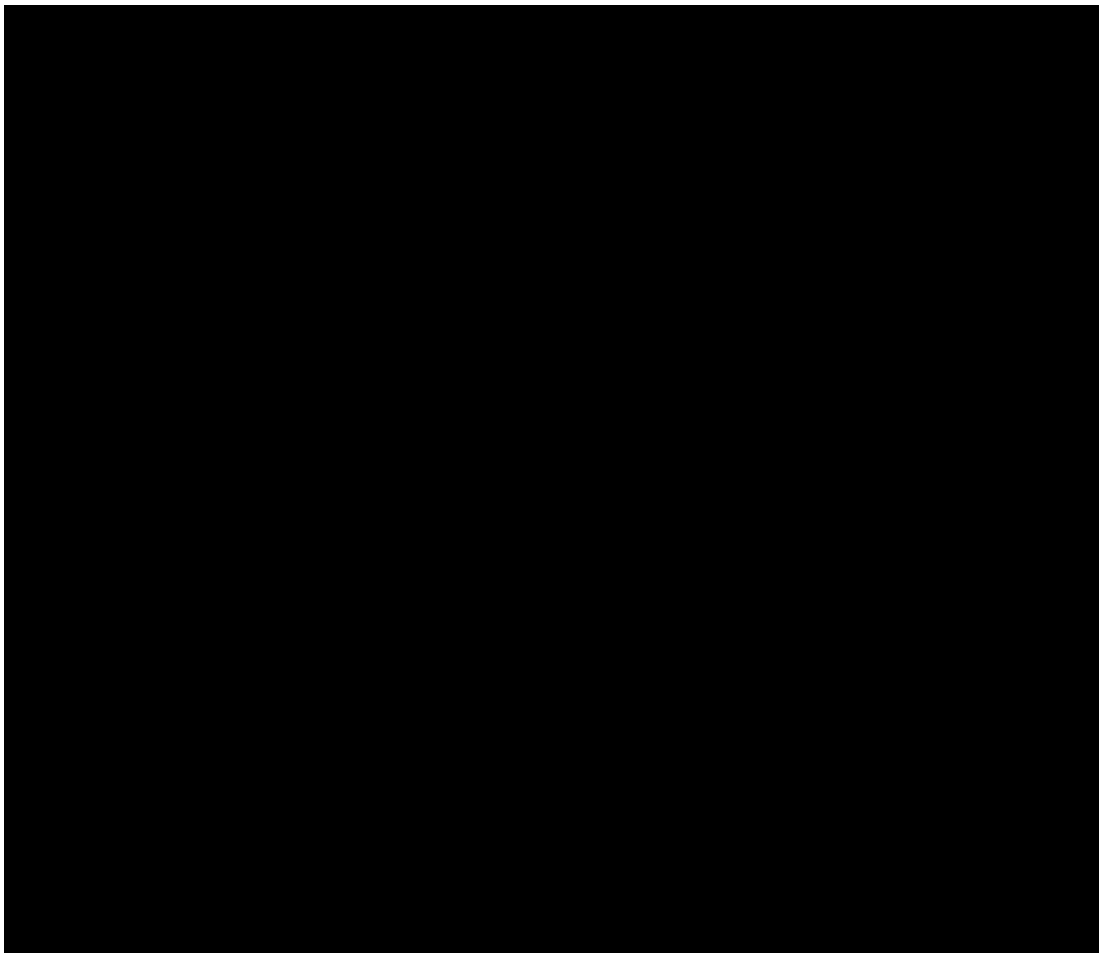

Fig 3 - LC-MS analysis – [redacted]

Blank 95% Ethanol – directly injected, without concentration

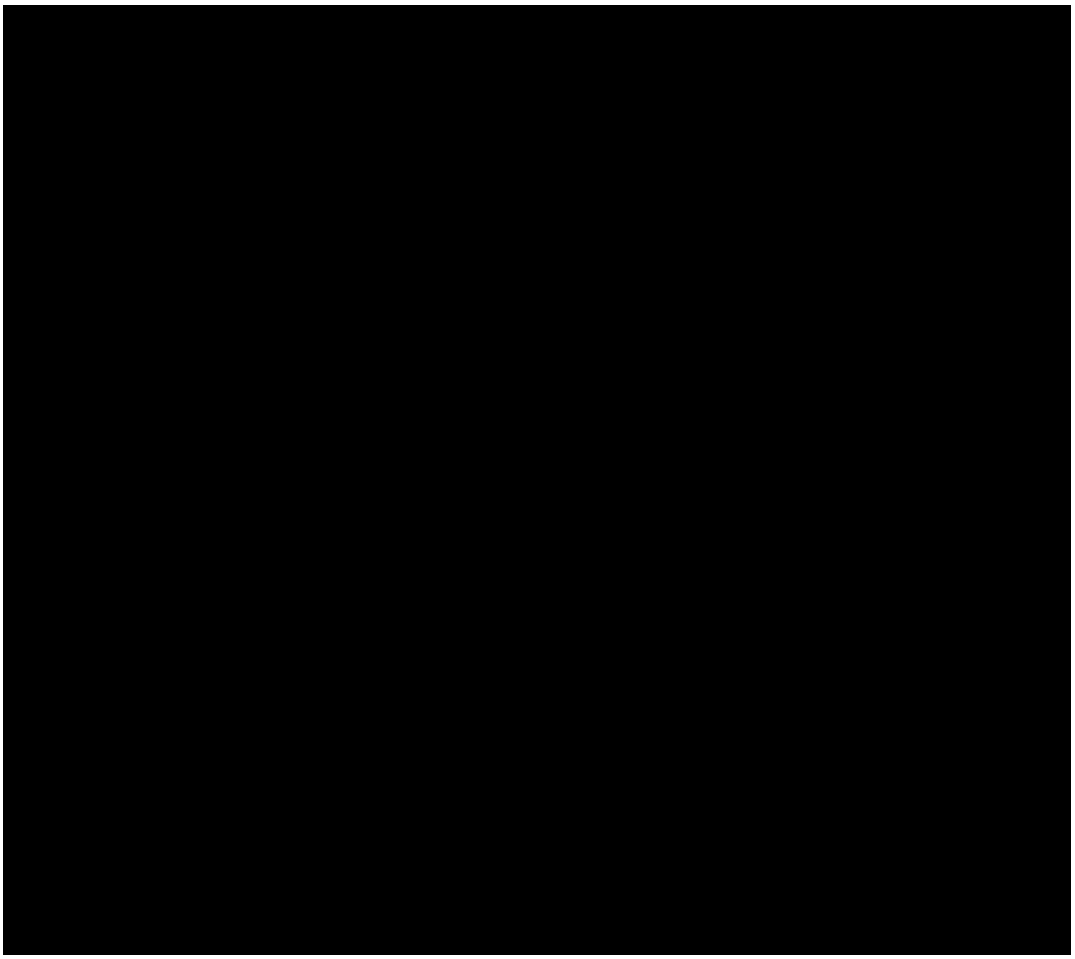

Fig 4 - LC-MS analysis – [redacted]

95% Ethanol sample extract (6 hr 60°C) directly injected, without concentration

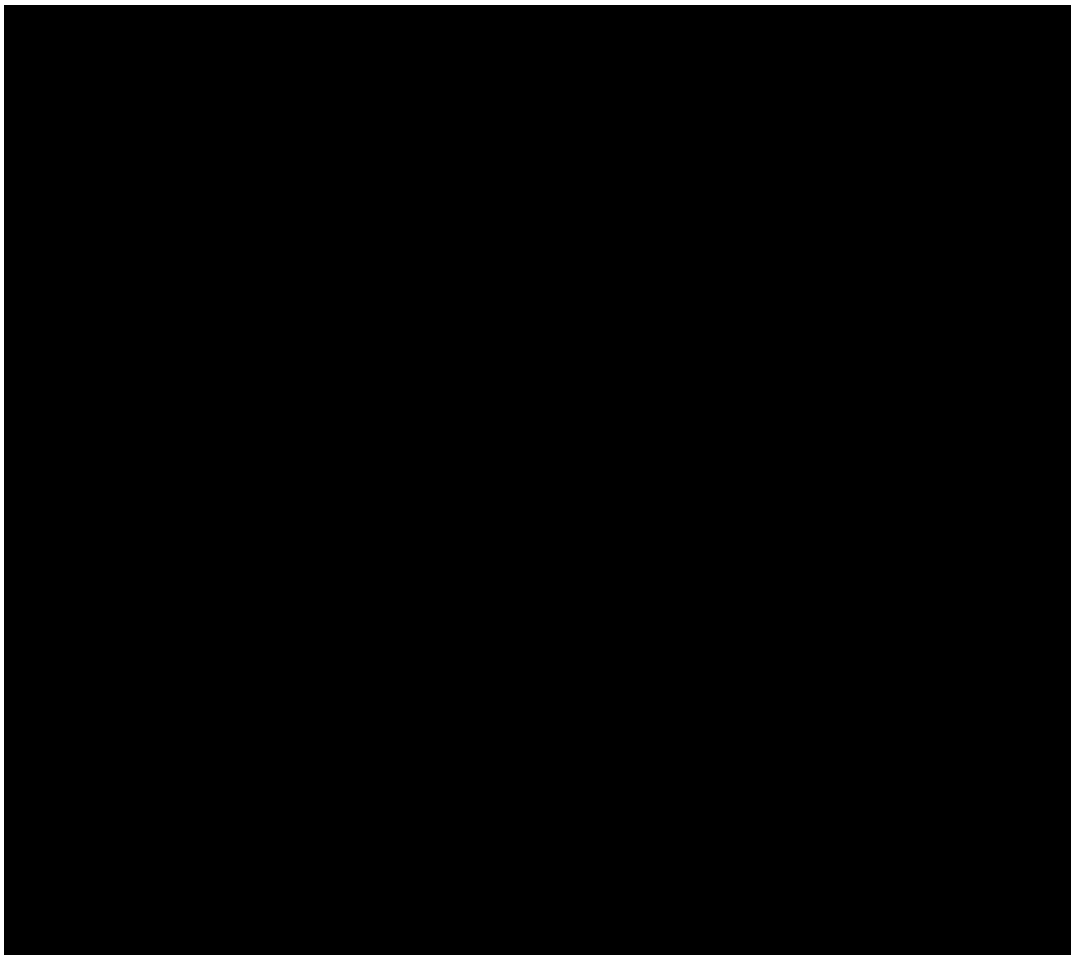

Fig 5 - LC-MS analysis – [redacted]

Blank 95% Ethanol - concentrated prior to analysis

Fig 6 - LC-MS analysis – [redacted]

95% Ethanol sample extract (6 hr 60°C), concentrated prior to analysis

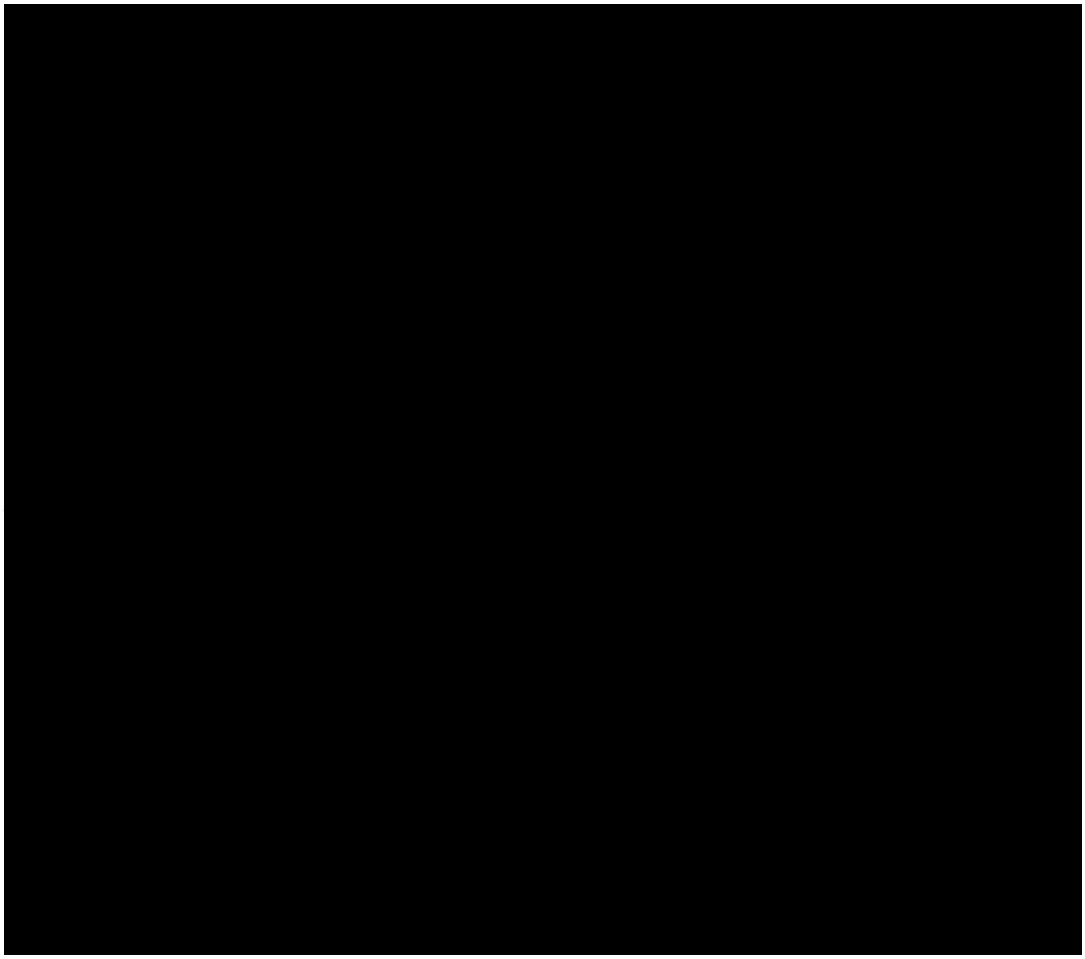

Fig 7 - LC-MS analysis – [redacted]

Standard solution Fluorolink 7800:7850 in 95% ethanol – 10 µg/ml

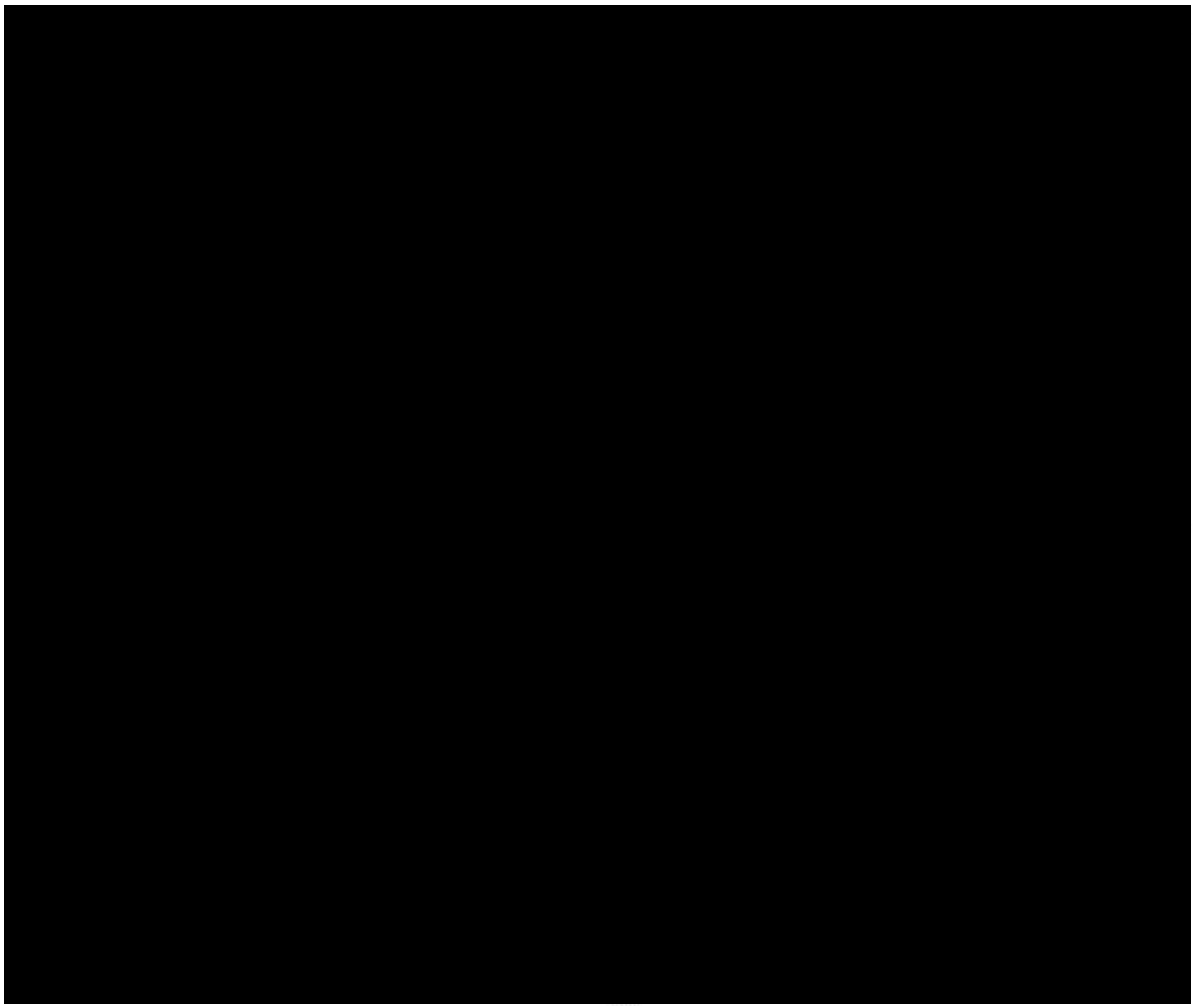

Fig 8 - LC-MS analysis – [redacted]

Standard solution Fluorolink 7800:7850 in 95% ethanol – 50 µg/ml

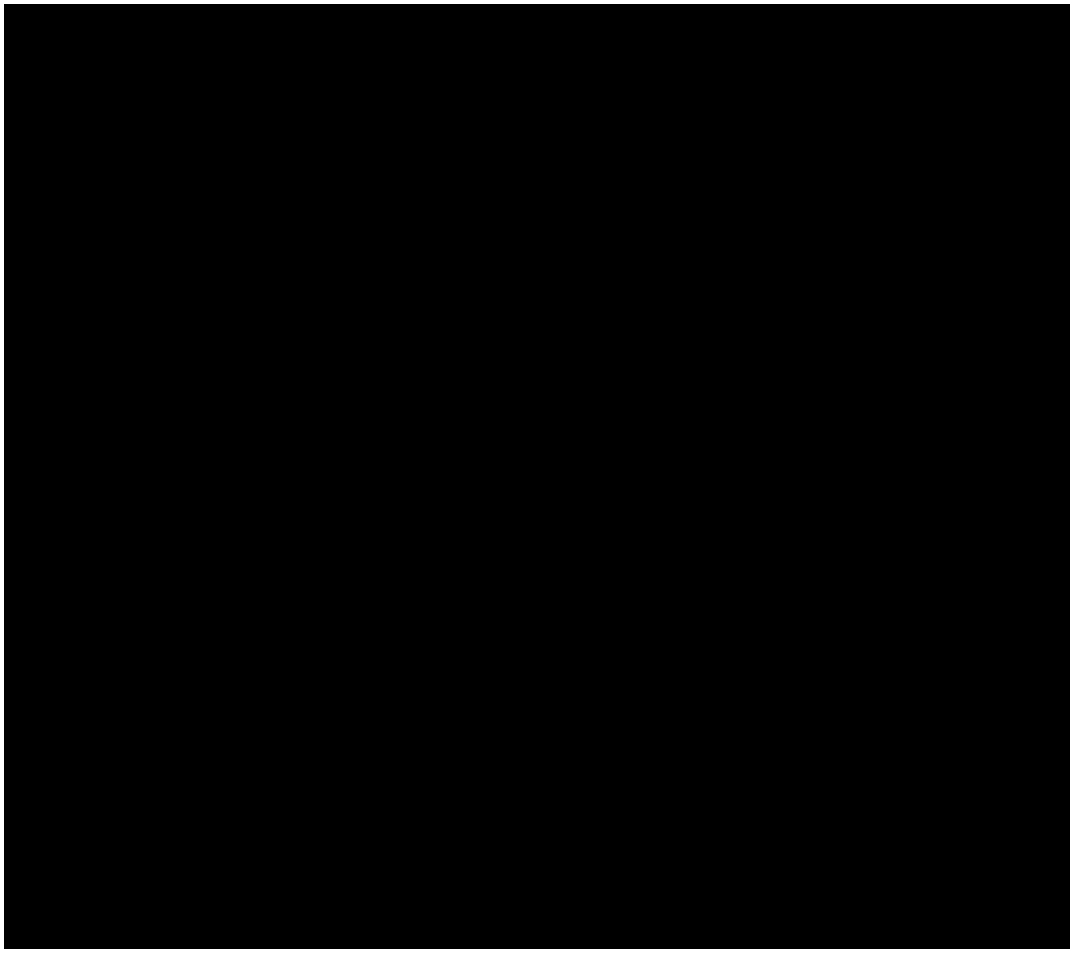

Fig 9 - LC-MS analysis – [redacted]

Blank 95% Ethanol – directly injected, without concentration

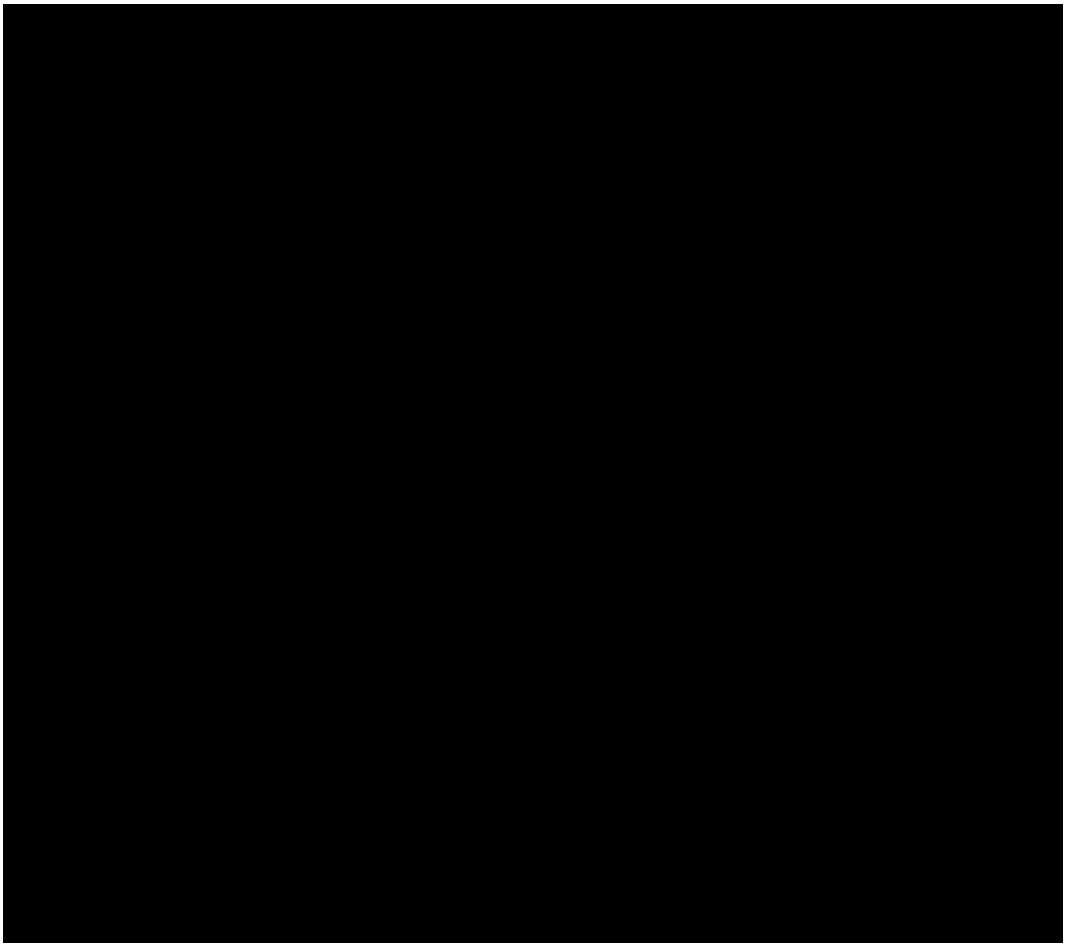

Fig 10 - LC-MS analysis – [redacted]

95% Ethanol sample extract (6 hr 60°C) directly injected, without concentration

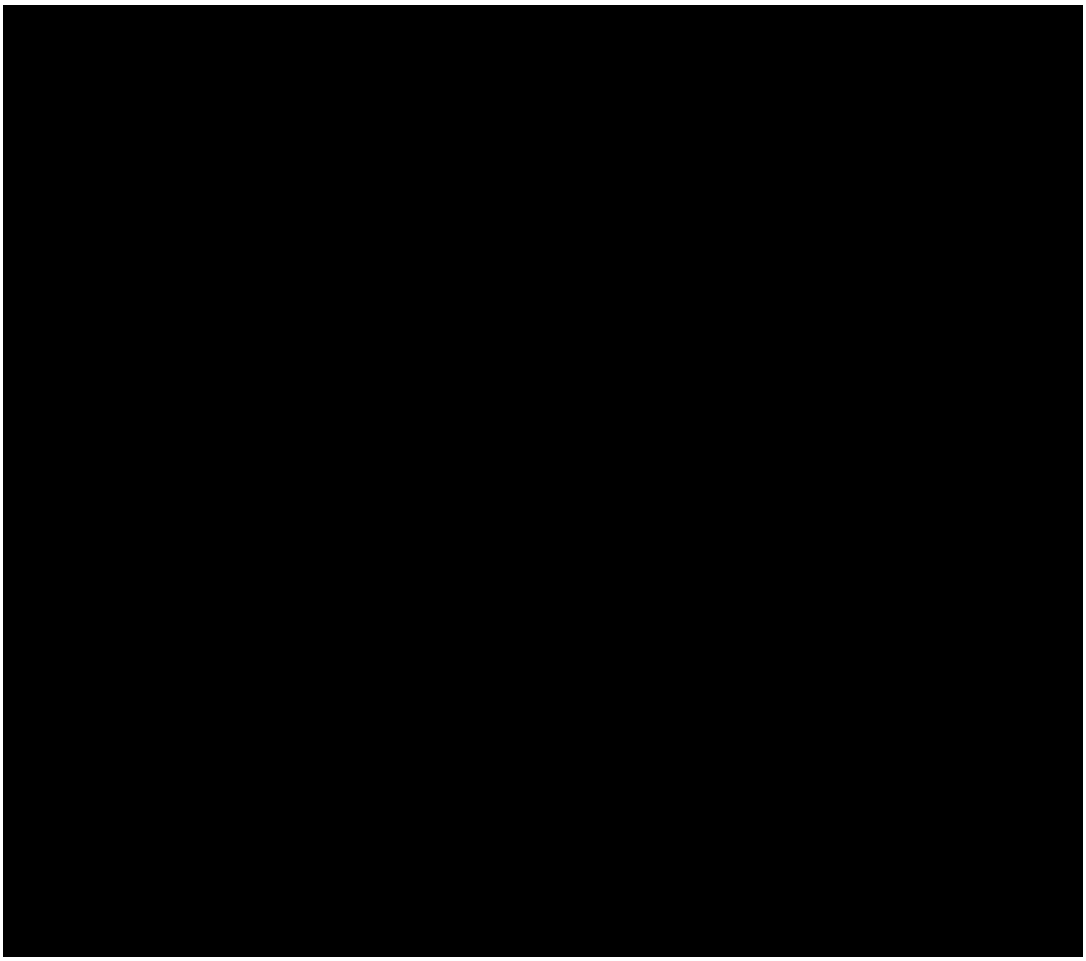

Fig 11 - LC-MS analysis – [redacted]

Blank 95% Ethanol, concentrated prior to injection

Fig 12 - LC-MS analysis – [redacted]

95% ethanol sample extract (6 hr 60°C), concentrated prior to injection

Fig 13 – GC-MS chromatogram

Standard solution Fluorolink 7800:7850 in 95% ethanol – 10 µg/ml

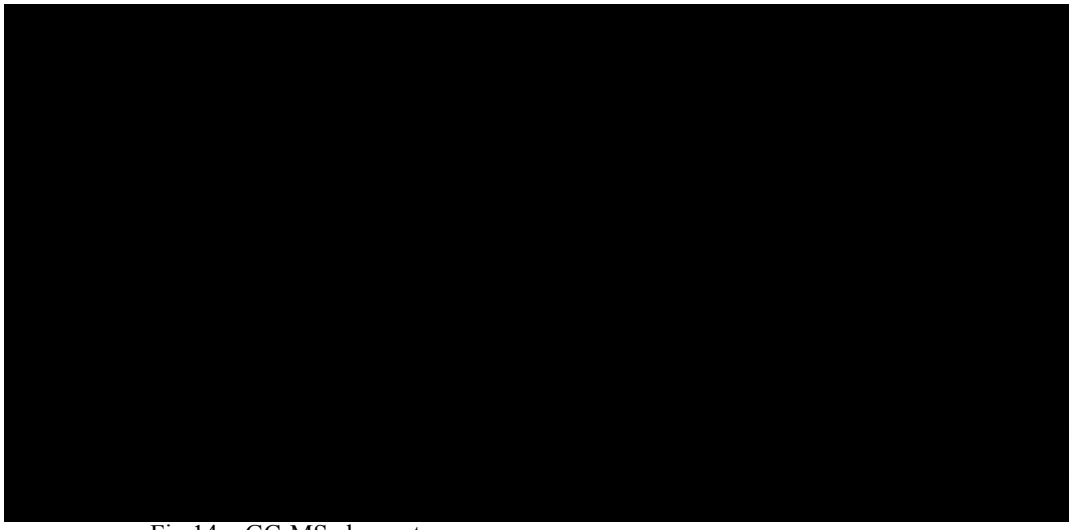

Fig 14 – GC-MS chromatogram

Standard solution Fluorolink 7800:7850 in 95% ethanol – 50 µg/ml

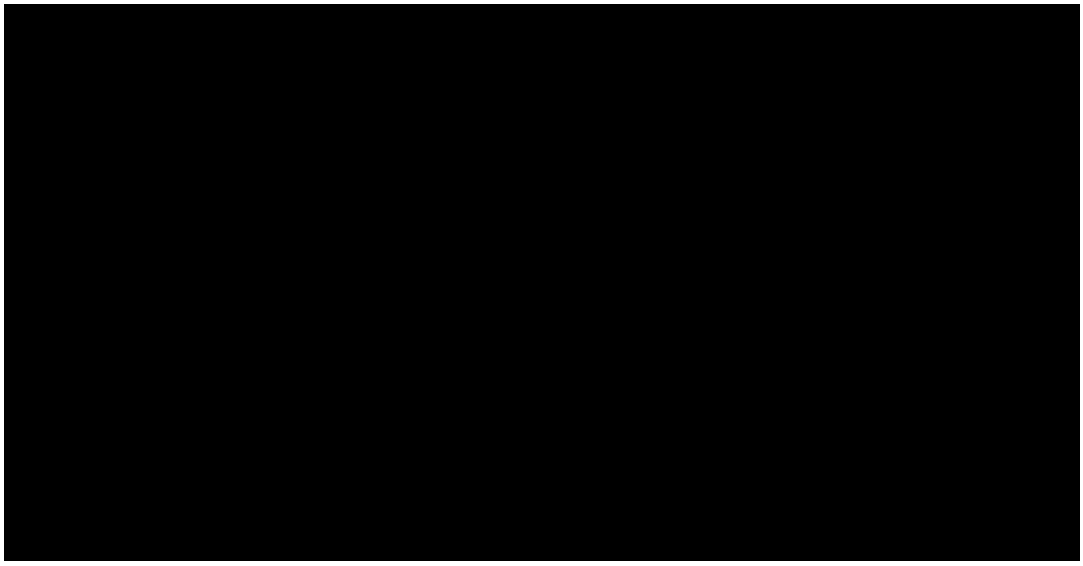

Fig. 15 – GC/MS chromatogram,

Blank 95% ethanol, directly injected without concentration

Fig. 16 – GC/MS chromatogram

95% ethanol sample extract (6 hr 60°C)– directly analysed, without concentration

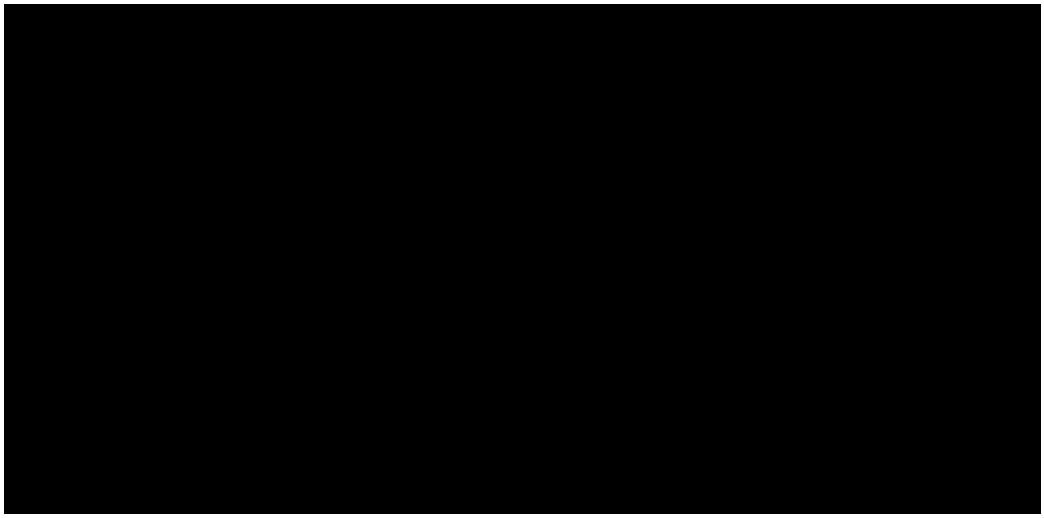

Fig. 17 – GC/MS chromatogram,

Blank 95% ethanol, concentrated prior to analysis

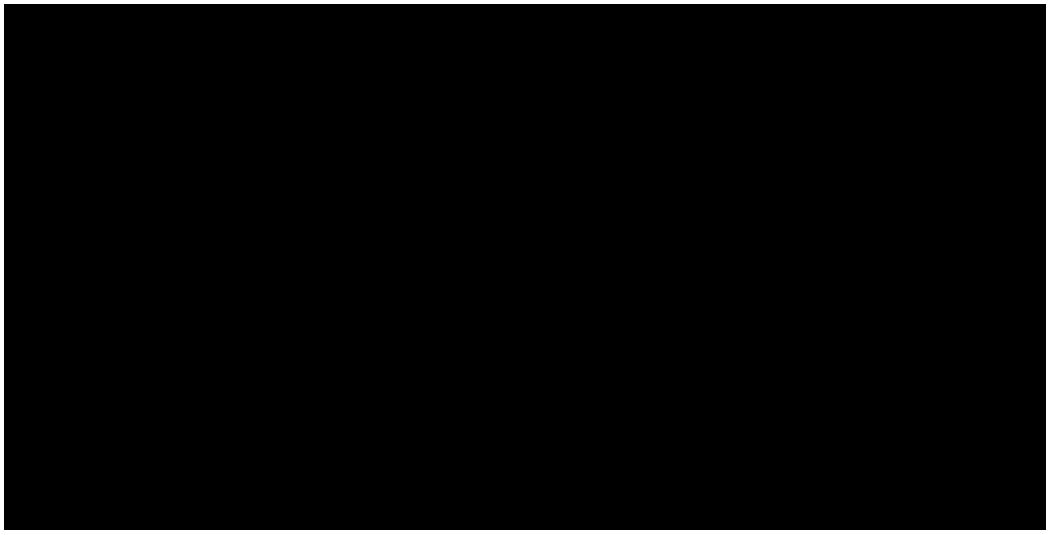

Fig. 18 – GC/MS chromatogram,

95% ethanol sample extract (6 hr 60°C), concentrated prior to analysis