

**SECTION 2**  
**TECHNICAL PART**

**2.4 Confirmation analysis by GC/C/IRMS**

**2.4.2 Isotopic ratio analysis**

LNDD	MODE OPÉRATOIRE	Codification : M-AN -41 Version : B Date :28/10/2005 1/2
<b>MODE OPERATOIRE D'ANALYSE POUR LA CONFIRMATION DE L'ORIGINE DES METABOLITES DE LA TESTOSTERONE PAR CPG/C/SMRI</b>		

**SPECIMEN**

**COLONNE**

Type: DB17-MS JW Scien 122.4732  
 Longueur: 30m  
 Diamètre interne: 0.25mm  
 Epaisseur du film: 0.25µm

ASSURANCE QUALITÉ  
LNDD

**INJECTION**

Mode: Splitless (insert splitless)  
 Température injecteur: 280°C  
 Volume injecté: 1µl-4µl  
 Solvants de rinçage ALS: Solvant A: Acétonitrile  
 Solvant B: Hexane

APPLICABLE le

28 OCT. 2005

**CONDITIONS GC**

Température initiale: 70°C pendant 1 min  
 Gradient de température: 70→271°C à 30°C/min  
 271°C→281°C à 0.6°C/min  
 281°C pendant 3 min  
 281→300°C à 5°C/min  
 Température finale: 300°C pendant 5 min  
 Temps d'analyse: 45 min  
 Pression constante: Ajuster le SI à environ 870s

**INTERFACE**

Piège à eau: -100°C  
 Ligne de transfert: 350°C  
 Four à combustion: 850°C

**CONFIDENTIEL**

**CONDITIONS SM**

Mode d'acquisition: ions 44, 45 et 46  
 Programmation de l'acquisition: Temps d'acquisition total:2580s  
 à 100s RG open  
 à 130s RG close  
 à 160s RG open  
 à 190s RG close  
 à 220s RG open  
 à 250s RG close  
 à 750s HS close  
 à 2000s HS open  
 à 2400s RG open  
 à 2430s RG close  
 à 2460s RG open  
 à 2490s RG close  
 à 2510s RG open  
 à 2540s RG close

Batch Data Processing Results

Data File Name : 230706  
 Autorun Setup File Name : 230706  
 Blank Subtraction : Disabled  
 Background Subtraction : Disabled  
 Reference Gas : Enabled  
 Ref Gas Delta (C13) : -34.50  
 Ref Gas Delta (O18) : -19.30  
 Current Time : 21:23:49  
 Current Date : 23/07/06

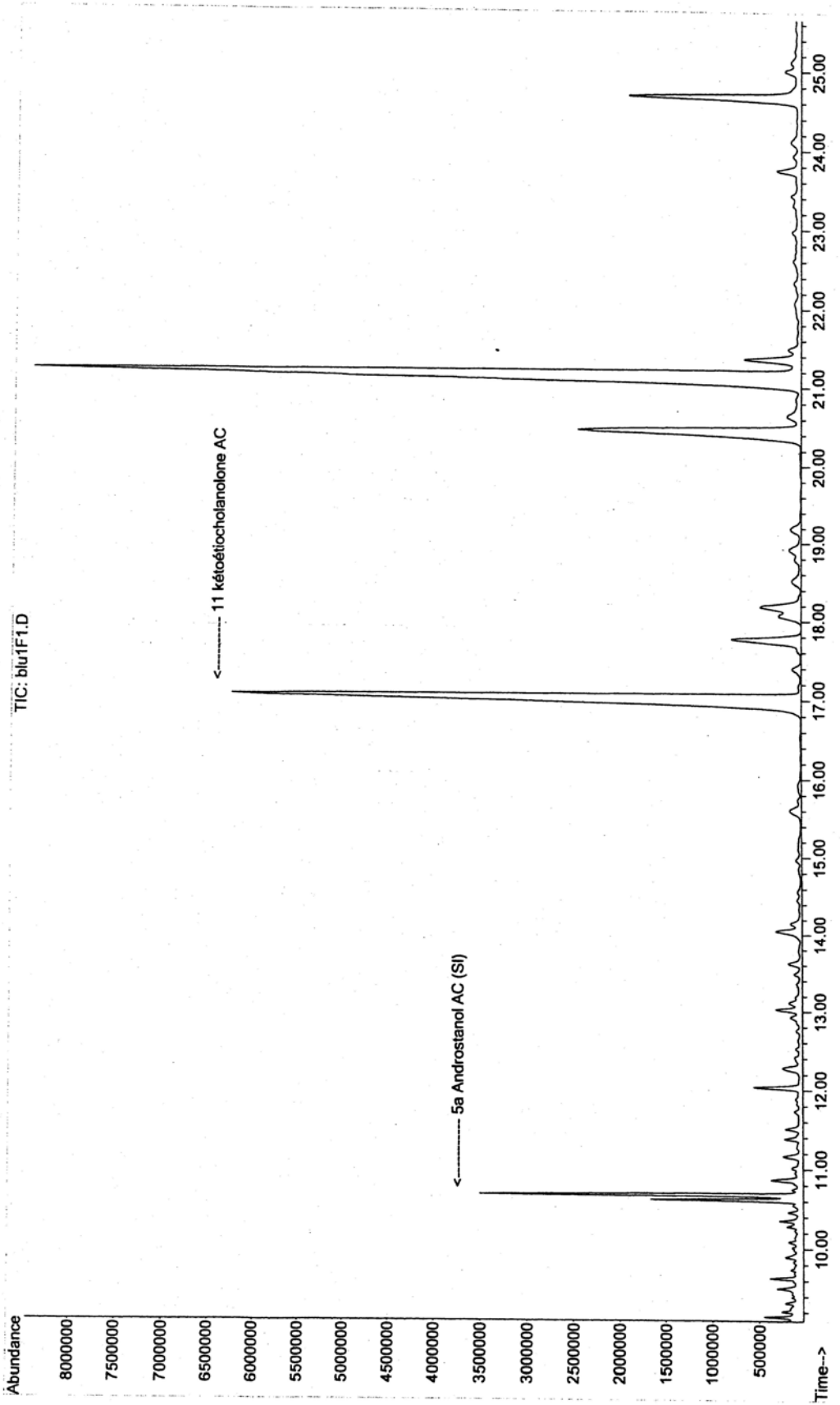
Sample Details		Elemental Isotopic			
No.	Name	Weight (mg)	Ref Type	% Comp (C)	Delta (C13) (O18)
1	stabilite 1	0.000	Sam		
2	stabilite 2	0.000	Sam		
3	stabilite 3	0.000	Sam		
4	Mix cal IRMS 003-1	0.000	Sam		
5	Mix cal IRMS 003-2	0.000	Sam		-31.51 -41.1
6	Mix cal IRMS 003-3	0.000	Sam		-32.22 -39.5
7	Mix cal Acetate 001A-100ng inj	0.000	Sam	0.000	-31.59 -40.3
8	Blu 1 pool 4 F3/45ul inj 2ul			0.000 Sam	-
9	178/07 995474 F3/45ul inj 2ul			0.000 Sam	-30
10	Blu 1 pool 4 F1/50ul inj 1ul			0.000 Sam	-3
11	178/07 995474 F1/50ul inj 1ul			0.000 Sam	-30
12	Blu 1 pool 4 F2/500ul inj 1ul			0.000 Sam	-3
13	178/07 995474 F2/400ul inj 1ul			0.000 Sam	-2
14	Mix Cal Acetate 001A-2	0.000	Sam	0.000	-25.21

Sample Details		Elemental Isotopic			
No.	Name	Weight (mg)	Ref Type	Atom % (C13)	Atom % XS (C13)
1	stabilite 1	0.000	Sam		
2	stabilite 2	0.000	Sam		
3	stabilite 3	0.000	Sam		
4	Mix cal IRMS 003-1	0.000	Sam	1.07659	-0.0346
5	Mix cal IRMS 003-2	0.000	Sam	1.07582	-0.0354
6	Mix cal IRMS 003-3	0.000	Sam	1.07651	-0.0347
7	Mix cal Acetate 001A-100ng inj			0.000 Sam	1.08310 -
8	Blu 1 pool 4 F3/45ul inj 2ul			0.000 Sam	1.07733 -0.
9	178/07 995474 F3/45ul inj 2ul			0.000 Sam	1.07699 -0
10	Blu 1 pool 4 F1/50ul inj 1ul			0.000 Sam	1.07809 -0.
11	178/07 995474 F1/50ul inj 1ul			0.000 Sam	1.07812 -0
12	Blu 1 pool 4 F2/500ul inj 1ul			0.000 Sam	1.07960 -0
13	178/07 995474 F2/400ul inj 1ul			0.000 Sam	1.07095 -
14	Mix Cal Acetate 001A-2	0.000	Sam	0.000	-25.21

Séquence vérifiée par : .....49.....

Remarques : .....

File : D:\Msd22\Juill06\2307\blu1F1.D  
Operator : 49  
Acquired : 23 Jul 2006 12:10 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name: Blu 1 F1  
Misc Info : Blanc urinaire 1 Pool 4 Fraction 1 dans 100µL  
Vial Number: 4



Data Processing Results

Data File Name : DATA\_010  
 Folder : 230706  
 Sample Name : Blu 1 pool 4 F1/50ul inj 1ul  
 Sample ID :  
 Sample Position : 5  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 13:11:34 Date : 23/07/06  
 Current Time : 13:56:19 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.633E-8	1.1780E-2	4.2529E-3
182.6	8.640E-8	1.1780E-2	4.2531E-3
242.7	8.674E-8	1.1780E-2	4.2530E-3
2423.5	8.603E-8	1.1779E-2	4.2523E-3
2483.5	8.553E-8	1.1779E-2	4.2524E-3
2533.5	8.673E-8	1.1780E-2	4.2528E-3

Std Dev Of Fit 1.5656E-7 1.9660E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	867.0	3.68E-9	1.5842E-8	1.1815E-2	4.1787E-3	-30.80	-58.95	-36.42	15
	1473.5	3.27E-9	3.4193E-8	1.1885E-2	4.1658E-3	-24.55	-59.30	-39.40	18
	1763.2	1.29E-9	1.4952E-8	1.1865E-2	4.1785E-3	-26.44	-58.27	-36.43	17
	1826.6	3.77E-9	4.6201E-8	1.1879E-2	4.1729E-3	-25.16	-57.89	-37.73	16

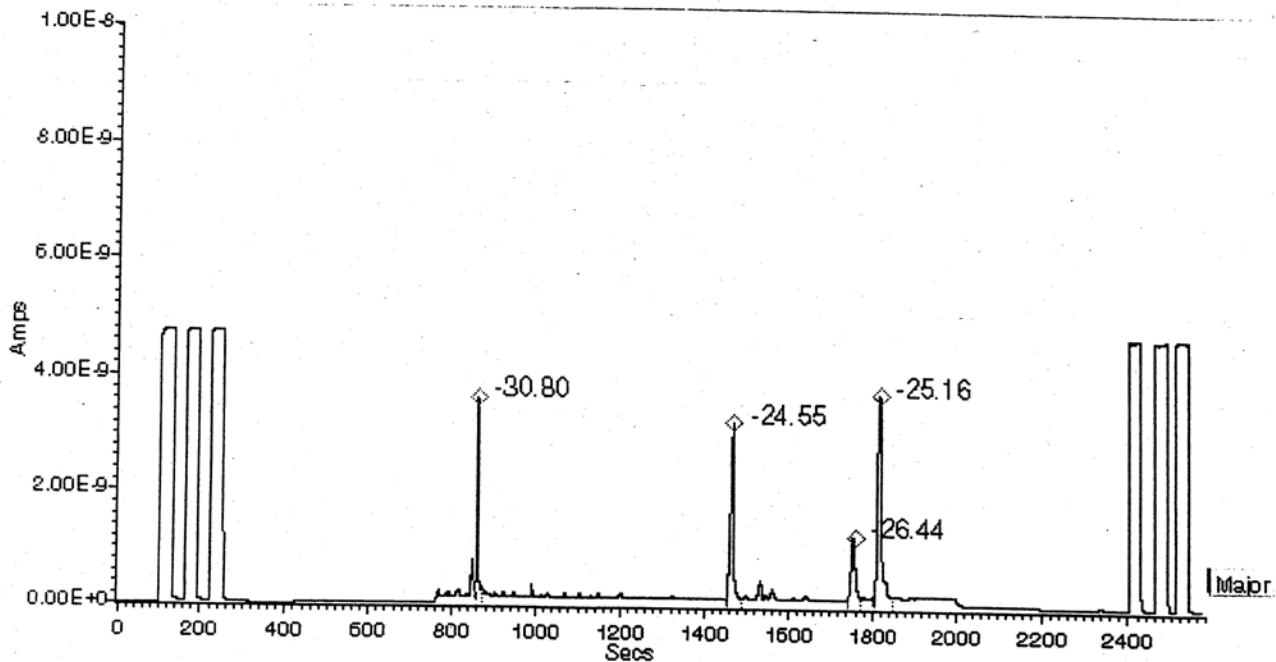
DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

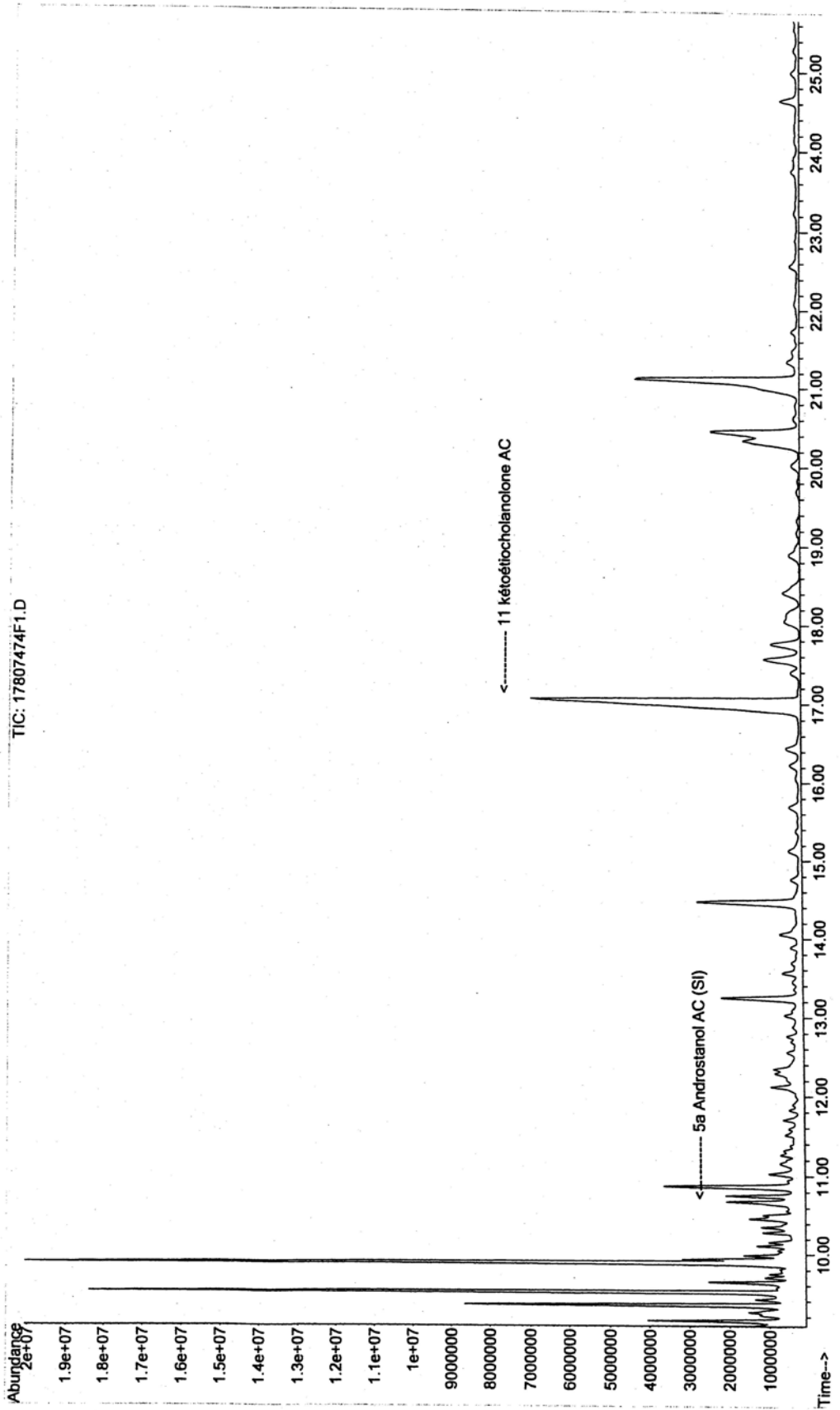
Data      Filename : DATA\_010      Folder : 230706  
            Date : 23/07/06      Time : 13:11:34  
            Comment : Blu 1 pool 4 F1/50ul inj 1ul:  
Parameters      Automatic DP Params

< Data Processing Main Graph

Graph Cursor Lines Window



File : D:\MsD22\Jul106\2307\17807474F1.D  
Operator : 49  
Acquired : 23 Jul 2006 12:42 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name: 178/07 995474 F1  
Misc Info : 178/07 995474 Fraction 1 dans 100µL  
Vial Number: 5



Data Processing Results

Data File Name : DATA\_011  
 Folder : 230706  
 Sample Name : 178/07 995474 F1/50ul inj 1ul  
 Sample ID :  
 Sample Position : 6  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 13:56:22 Date : 23/07/06  
 Current Time : 12:23:08 Date : 24/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.557E-8	1.1780E-2	4.2530E-3
182.6	8.541E-8	1.1779E-2	4.2529E-3
242.7	8.559E-8	1.1779E-2	4.2528E-3
2423.5	8.570E-8	1.1780E-2	4.2528E-3
2483.5	8.477E-8	1.1779E-2	4.2526E-3
2533.5	8.552E-8	1.1779E-2	4.2525E-3

Std Dev Of Fit 4.6711E-7 1.1648E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	778.0	1.02E-8	5.1128E-8	1.1786E-2	4.1817E-3	-33.40	-55.27	-35.72	5
	867.0	4.02E-9	2.3358E-8	1.1807E-2	4.1997E-3	-31.64	-54.92	-31.57	6
	881.6	2.01E-9	1.9104E-8	1.1783E-2	4.2233E-3	-33.95	-54.82	-26.11	6
	1236.3	1.47E-9	1.4752E-8	1.1868E-2	4.2016E-3	-26.35	-53.09	-31.14	9
	1478.2	4.55E-9	5.1339E-8	1.1890E-2	4.1691E-3	-24.10	-51.64	-38.62	10
	1764.6	1.56E-9	1.7786E-8	1.1872E-2	4.1715E-3	-25.78	-49.65	-38.06	10
	1824.1	2.65E-9	2.5363E-8	1.1878E-2	4.1684E-3	-25.15	-49.23	-38.77	10



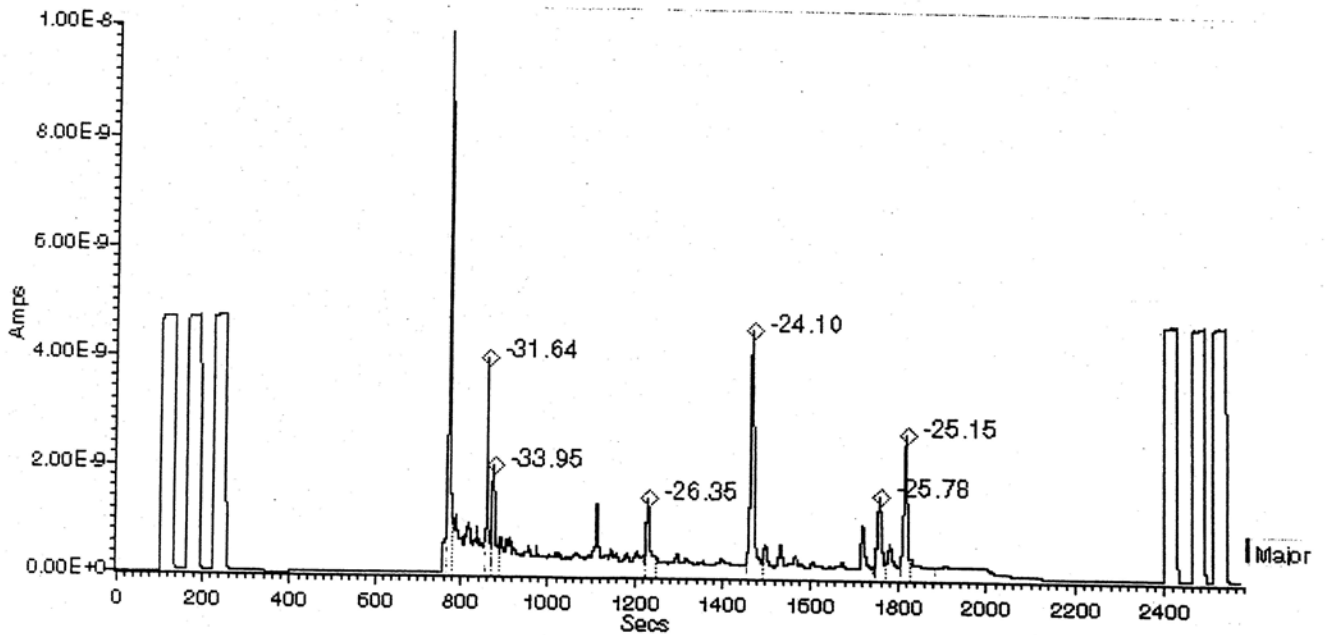
DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

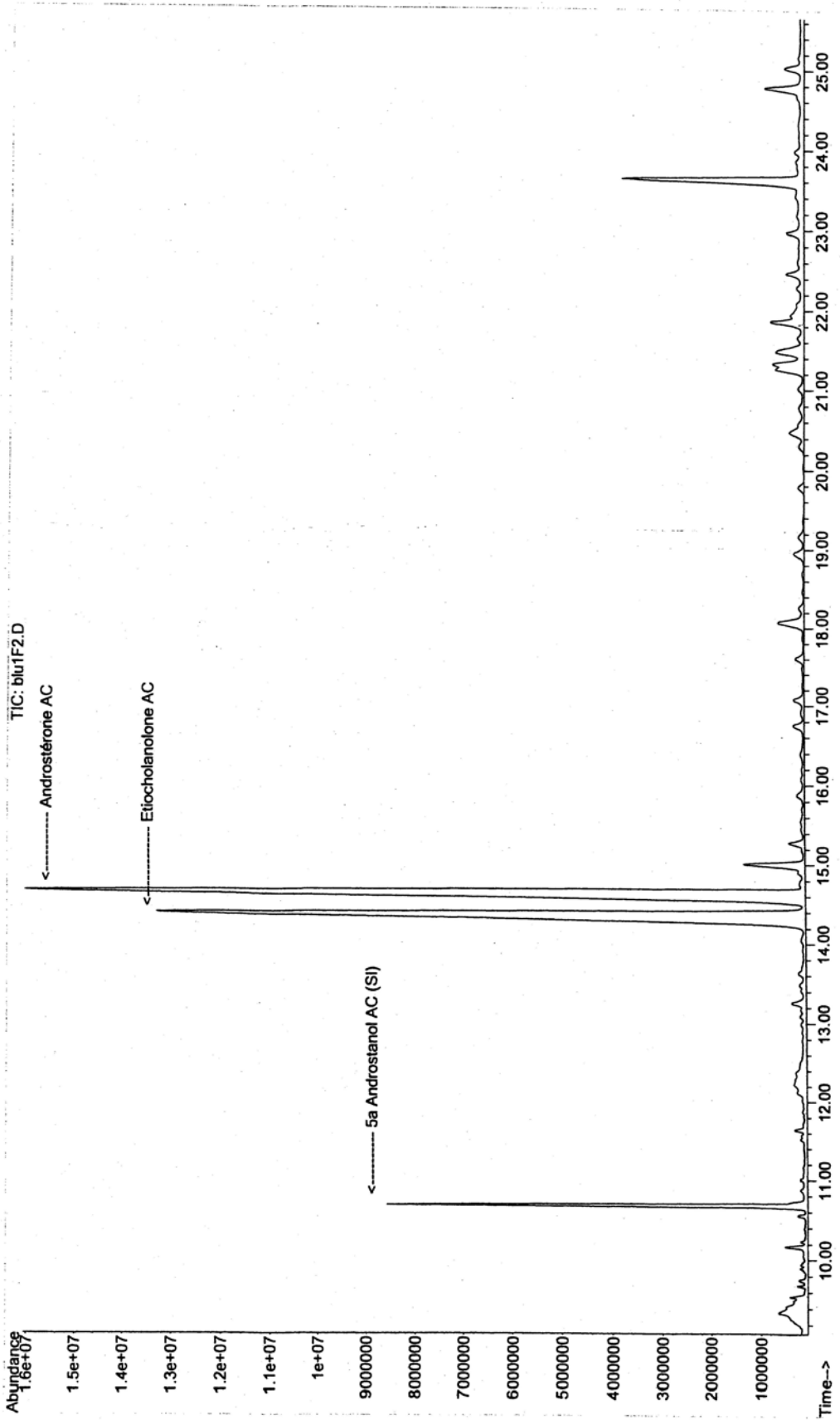
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            Date : 23/07/06      Time : 13:56:22  
            Comment : 178/07 995474 F1/50ul inj 1ul:  
Parameters      Automatic DP Params

DP Data Processing Main Graph

Graph Cursor Lines Window



File : D:\Msd22\Juil06\2307\blu1F2.D  
Operator : 49  
Acquired : 23 Jul 2006 13:15 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name: Blu 1 F2  
Misc Info : Blanc urinaire 1 Pool 4 Fraction 2 dans 400µL  
Vial Number: 6



Data Processing Results

Data File Name : DATA\_012  
 Folder : 230706  
 Sample Name : Blu 1 pool 4 F2/500ul inj 1ul  
 Sample ID :  
 Sample Position : 7  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 14:41:06 Date : 23/07/06  
 Current Time : 16:02:44 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.5	8.634E-8	1.1779E-2	4.2525E-3
182.6	8.646E-8	1.1779E-2	4.2529E-3
242.6	8.648E-8	1.1779E-2	4.2529E-3
2423.4	8.572E-8	1.1779E-2	4.2526E-3
2483.4	8.565E-8	1.1778E-2	4.2526E-3
2533.5	8.561E-8	1.1779E-2	4.2529E-3

Std Dev Of Fit 2.0409E-7 1.7605E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	868.0	2.74E-9	1.4334E-8	1.1823E-2	4.1667E-3	-29.94	-65.47	-39.17	21
	1231.7	4.52E-9	3.4691E-8	1.1876E-2	4.1668E-3	-25.34	-63.44	-39.15	21
	1257.2	5.33E-9	4.1709E-8	1.1880E-2	4.1670E-3	-24.98	-63.15	-39.11	21

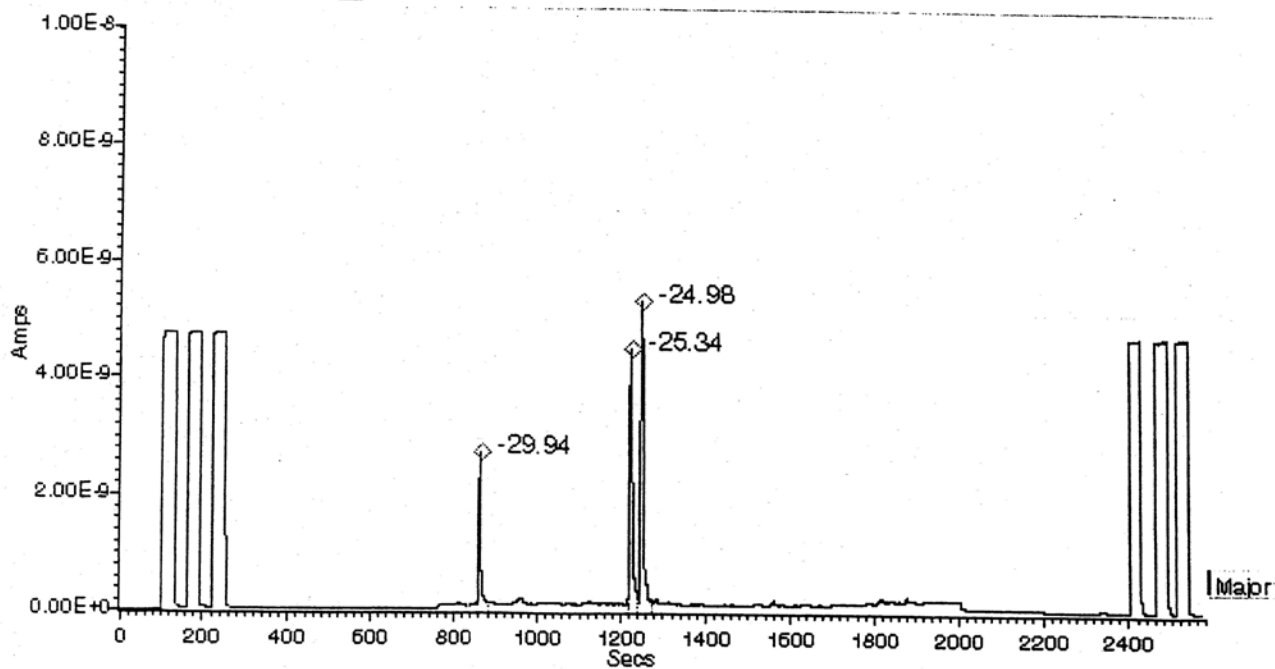
DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

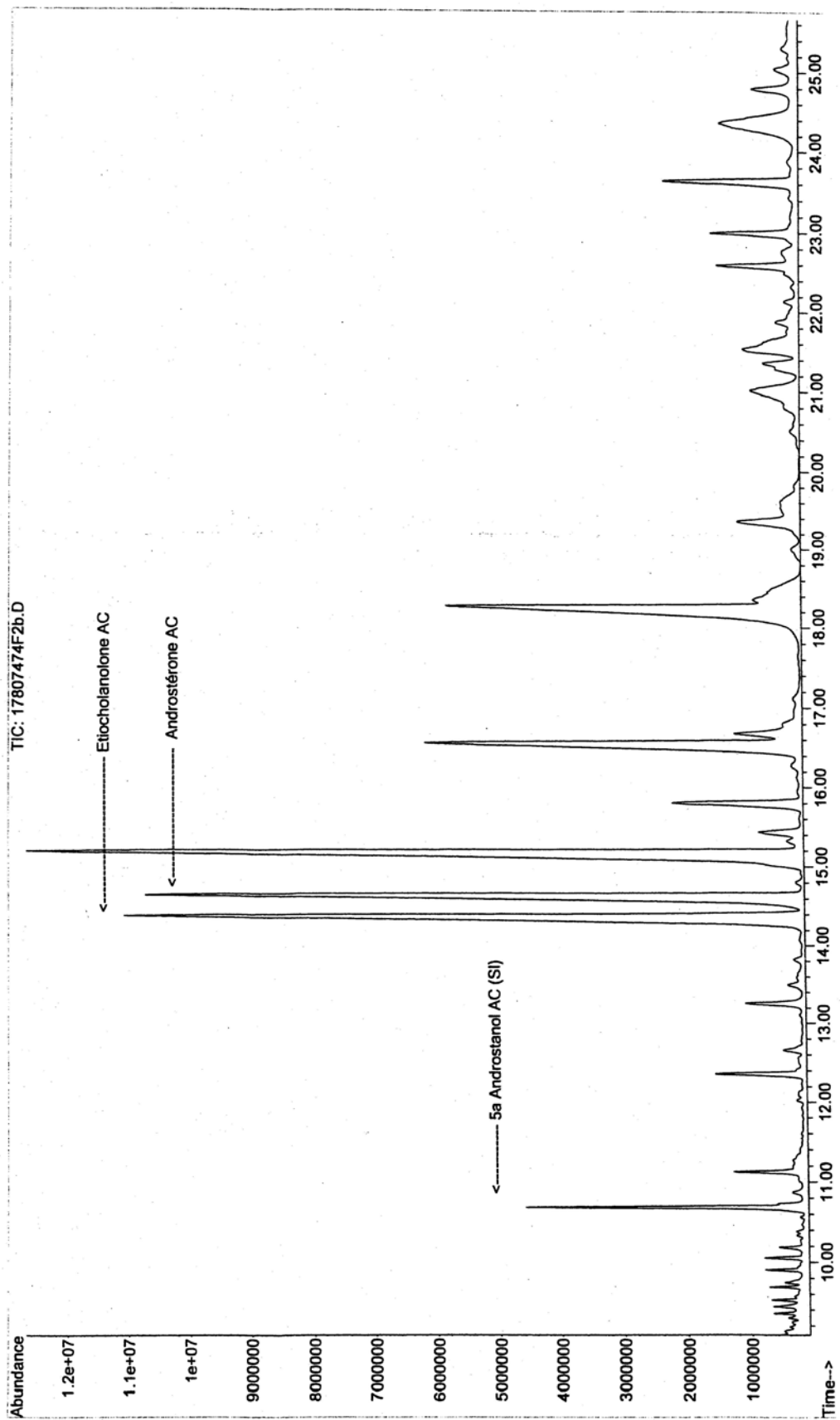
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                  Date : 23/07/06           Time : 14:41:06  
                  Comment : Blu 1 pool 4 F2/500ul inj 1ul:  
Parameters     Automatic DP Params

Data Processing Main Graph

Graph Cursor Lines Window



File : D:\Msd22\Juil06\2307\17807474F2b.D  
Operator : 49  
Acquired : 23 Jul 2006 14:33 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name: 178/07 995474 F2  
Misc Info : 178/07 995474 Fraction 2 dans 400uL  
Vial Number: 7



Data Processing Results

Data File Name : DATA\_013  
 Folder : 230706  
 Sample Name : 178/07 995474 F2/400ul inj 1ul  
 Sample ID :  
 Sample Position : 8  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 15:25:49 Date : 23/07/06  
 Current Time : 16:10:31 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.603E-8	1.1780E-2	4.2535E-3
182.6	8.588E-8	1.1779E-2	4.2537E-3
242.6	8.578E-8	1.1779E-2	4.2536E-3
2423.5	8.471E-8	1.1779E-2	4.2525E-3
2483.5	8.452E-8	1.1778E-2	4.2521E-3
2533.5	8.511E-8	1.1777E-2	4.2522E-3

Std Dev Of Fit 4.5694E-7 1.4227E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	866.0	2.17E-9	9.6593E-9	1.1822E-2	4.1703E-3	-30.07	-63.69	-38.44	18
	1229.7	3.95E-9	3.1256E-8	1.1863E-2	4.1661E-3	-26.43	-60.89	-39.38	18
	1254.3	3.39E-9	2.5932E-8	1.1849E-2	4.1704E-3	-27.71	-60.19	-38.39	18
	1288.3	3.55E-9	2.9815E-8	1.1797E-2	4.1768E-3	-32.28	-59.25	-36.88	17

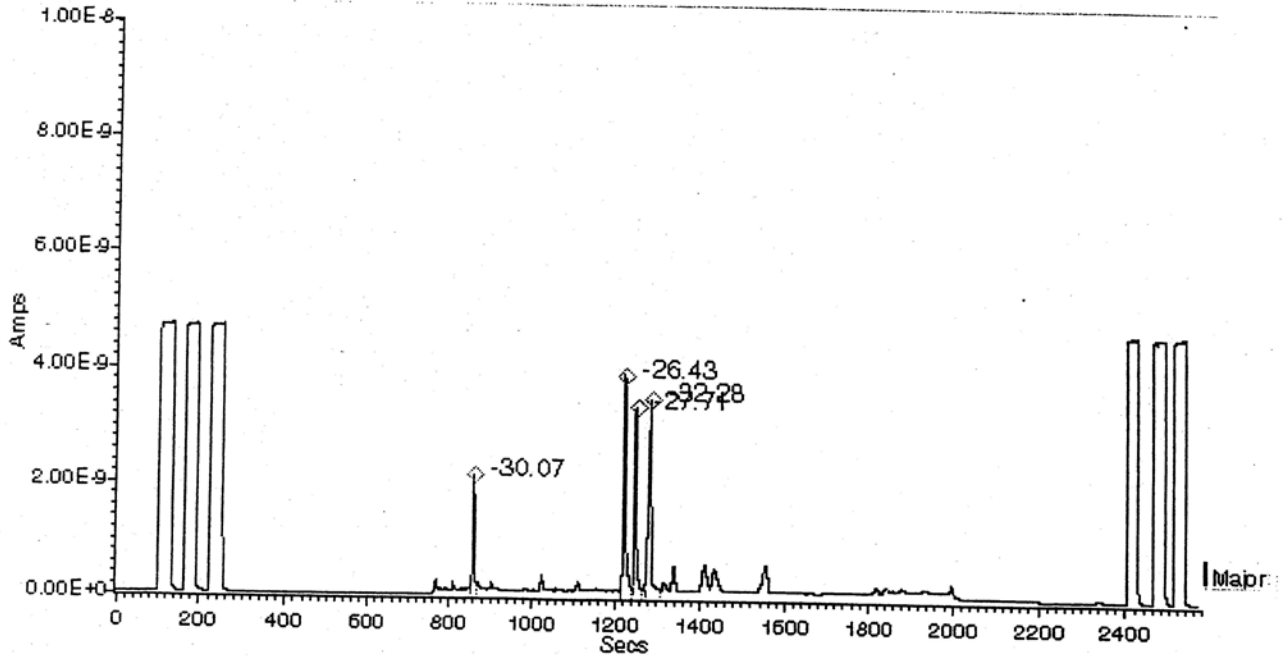
DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

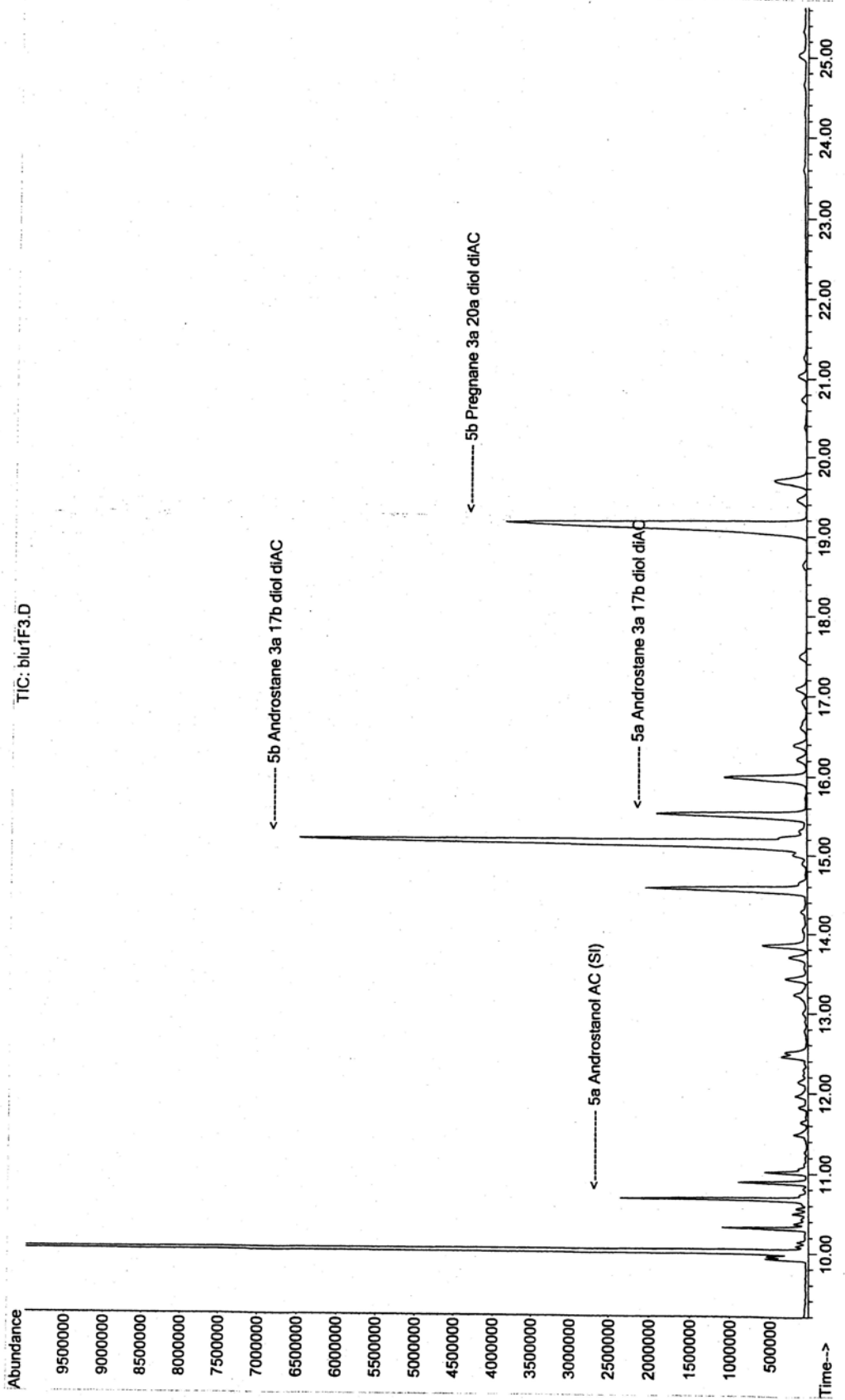
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            Comment : 178/07 995474 F2/400ul inj 1ul  
Parameters      Automatic DP Params

Data Processing Main Graph

Graph Cursor Lines Window



File : D:\MsD22\Juil106\2307\blu1F3.D  
Operator : 49  
Acquired : 23 Jul 2006 11:00 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name : Blu 1 F3  
Misc Info : Blanc urinaire 1 Pool 4 Fraction 3 dans 100µL  
Vial Number: 2





Data Processing Results

Data File Name : DATA\_008  
 Folder : 230706  
 Sample Name : Blu 1 pool 4 F3/45ul inj 2ul  
 Sample ID :  
 Sample Position : 3  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 11:40:11 Date : 23/07/06  
 Current Time : 12:28:05 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.660E-8	1.1780E-2	4.2525E-3
182.6	8.668E-8	1.1781E-2	4.2527E-3
242.6	8.673E-8	1.1781E-2	4.2531E-3
2423.5	8.560E-8	1.1783E-2	4.2534E-3
2483.5	8.558E-8	1.1782E-2	4.2529E-3
2533.5	8.621E-8	1.1782E-2	4.2533E-3

Std Dev Of Fit                      5.9183E-7                      2.6505E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	798.5	2.00E-8	1.2123E-7	1.1616E-2	4.4640E-3	-50.60	-61.70	29.47	9
	867.4	6.17E-9	3.4892E-8	1.1822E-2	4.2211E-3	-30.66	-62.20	-26.65	11
	1244.7	2.49E-9	2.1148E-8	1.1848E-2	4.1951E-3	-28.25	-63.83	-32.67	18
	1306.2	7.10E-9	6.5412E-8	1.1854E-2	4.1696E-3	-27.54	-63.93	-38.55	19
	1336.6	2.32E-9	1.8245E-8	1.1845E-2	4.1806E-3	-28.40	-63.99	-36.03	19
	1375.6	1.42E-9	1.2239E-8	1.1852E-2	4.1854E-3	-27.78	-64.02	-34.91	19
	1651.5	3.59E-9	3.9165E-8	1.1864E-2	4.1692E-3	-26.65	-63.59	-38.67	20

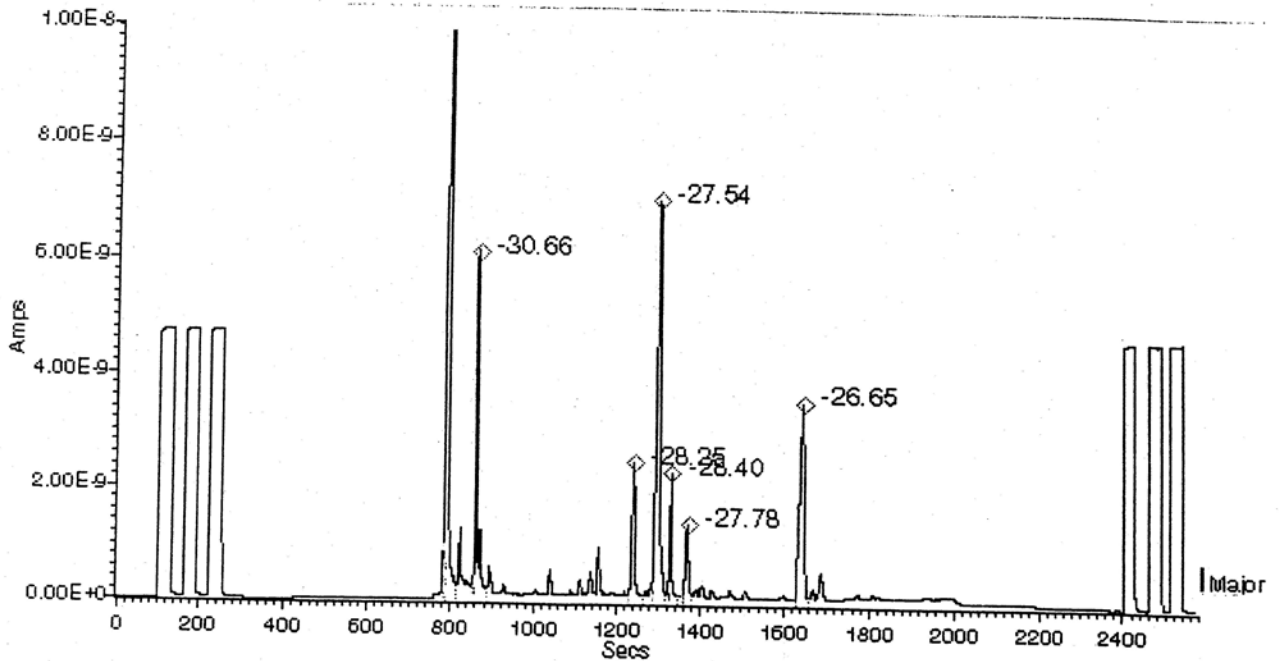
DP **Optima GC 1.67-2 - Manual DP**

**File Edit View Calculate Report Parameters Status Help**

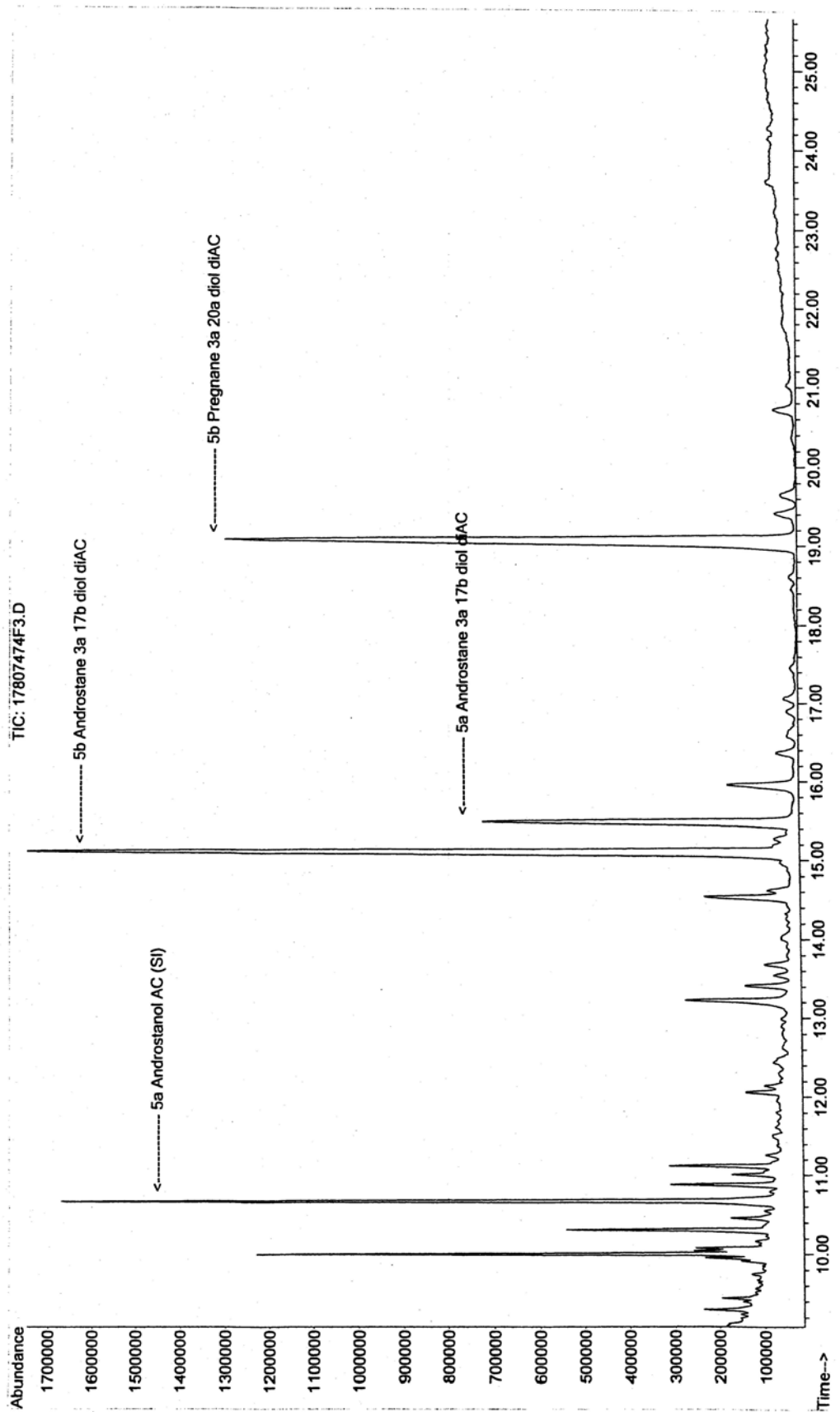
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                  Date : 23/07/06           Time : 11:40:11  
                  Comment : Blu 1 pool 4 F3/45ul inj 2ul:  
Parameters     Automatic DP Params

**Data Processing Main Graph**

**Graph Cursor Lines Window**



File : D:\Msdd22\Jui106\2307\17807474F3.D  
Operator : 49  
Acquired : 23 Jul 2006 11:33 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name : 178/07 995474 F3  
Misc Info : 178/07 995474 Fraction 3 dans 400uL  
Vial Number: 3



Data Processing Results

Data File Name : DATA\_009  
 Folder : 230706  
 Sample Name : 178/07 995474 F3/45ul inj 2ul  
 Sample ID :  
 Sample Position : 4  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 12:24:59 Date : 23/07/06  
 Current Time : 16:08:12 Date : 23/07/06

Analysis of Reference Gas Data  
 Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.494E-8	1.1782E-2	4.2529E-3
182.6	8.494E-8	1.1782E-2	4.2530E-3
242.6	8.494E-8	1.1781E-2	4.2527E-3
2423.5	8.443E-8	1.1780E-2	4.2518E-3
2483.5	8.453E-8	1.1779E-2	4.2517E-3
2533.5	8.566E-8	1.1779E-2	4.2520E-3

Std Dev Of Fit 5.6232E-7 1.7469E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	795.1	5.07E-9	2.5669E-8	1.1880E-2	4.2100E-3	-25.45	-55.46	-29.16	5
	827.1	2.21E-9	1.0385E-8	1.1883E-2	4.2270E-3	-25.34	-55.50	-25.22	6
	867.4	6.75E-9	3.0380E-8	1.1826E-2	4.1857E-3	-30.05	-55.38	-34.74	7
	1304.7	5.53E-9	4.6362E-8	1.1838E-2	4.1673E-3	-28.82	-53.62	-38.95	11
	1337.2	2.59E-9	2.1591E-8	1.1800E-2	4.1700E-3	-32.12	-53.42	-38.31	12
	1652.0	3.25E-9	3.7635E-8	1.1862E-2	4.1682E-3	-26.61	-51.12	-38.72	12

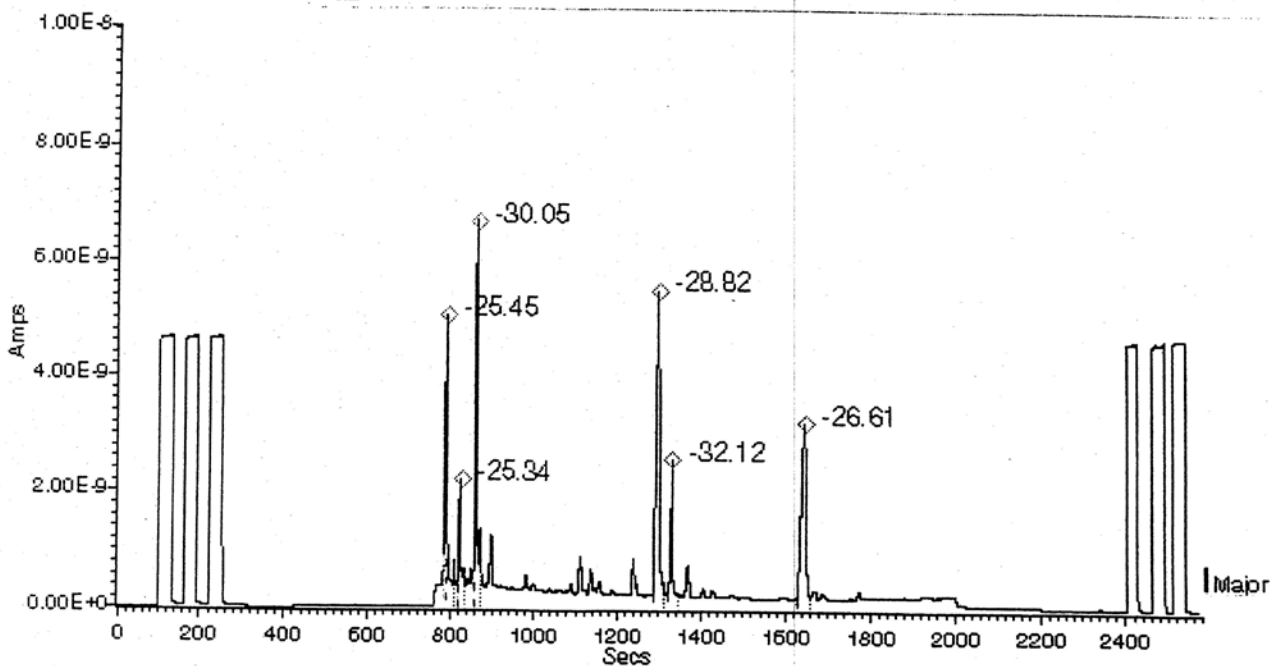
DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_009      Folder : 230706  
            Date : 23/07/06      Time : 12:24:59  
            Comment : 178/07 995474 F3/45ul inj 2ul :  
Parameters      Automatic DP Params

Data Processing Main Graph

Graph Cursor Lines Window



LNDD	ENREGISTREMENT	Codification: E-CC-10 Version: C Date: 09/05/2006 1/2
<b>VERIFICATION DES PERFORMANCES INSTRUMENTALES EN CONFIRMATION CG/IRMS</b>		

Numéro d'échantillon : ..... 178107 ..... 995474 .....  
 Numéro d'identification de l'appareil : ..... 150651NF1 .....  
 Instruction de confirmation : ..... I... CONF 3.1 .....

**1. Tune**

Spécification : plateau du peak Centre  $\geq 10$  V

Tune conforme :            oui             non

**2. Stabilité de l'instrument**

Spécification: écart mesuré entre valeur maximale et valeur minimale du ratio 2/1  $\leq 0.5$  %

Stabilité conforme :            oui             non

**3. Précision de l'instrument**

Code de la solution Mix Cal IRMS: ..... 003 .....  
Valeurs obtenues (%) pour 3 injections:

	Décane	Undécane	Dodécane	Méthyldécanoate
Moyenne	-31.61	-31.46	-31.01	-31.67
Ecart-type	0.12	0.19	0.10	0.13

Spécification: écart-type d'au moins 3 alcanes  $\leq 0.5$  %

Précision conforme :            oui             non

LNDD	ENREGISTREMENT	Codification : E-CC-10 Version : C Date : 09/05/2006 2/2
<b>VERIFICATION DES PERFORMANCES INSTRUMENTALES EN CONFIRMATION CG/C/IRMS</b>		

**4. Calibration de l'instrument**

Code de la solution Mix Cal Acétate:.....003.....

**Valeurs obtenues (%):**

	5a Androstanol AC	Etiocolanolone AC	5b Androstanediol diAC	11 Kétoetiocolanolone AC
Data 007	-30,59	-20,01	-33,70	-16,69
Data 14	-30,56	-20,22	-33,90	-16,76

**Intervalle de valeurs acceptables:**

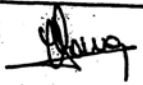

	5a Androstanol AC	Etiocolanolone AC	5b Androstanediol diAC	11 Kétoetiocolanolone AC
Valeurs théoriques	-30.46	-19.91	-33.81	-16.30
Valeurs théoriques + 0.5%	-29.96	-19.41	-33.31	-15.80
Valeurs théoriques - 0.5%	-30.96	-20.41	-34.31	-16.80

Résultats conformes :      oui       non

**Résultats : CONFORME / NON CONFORME**  
Rayer la mention inutile

Observations:

**Validation**

Opérateur		Responsable	
Date	Code et Visa	Date	Code et Visa
24/07/06	49 	24/07/06	19 

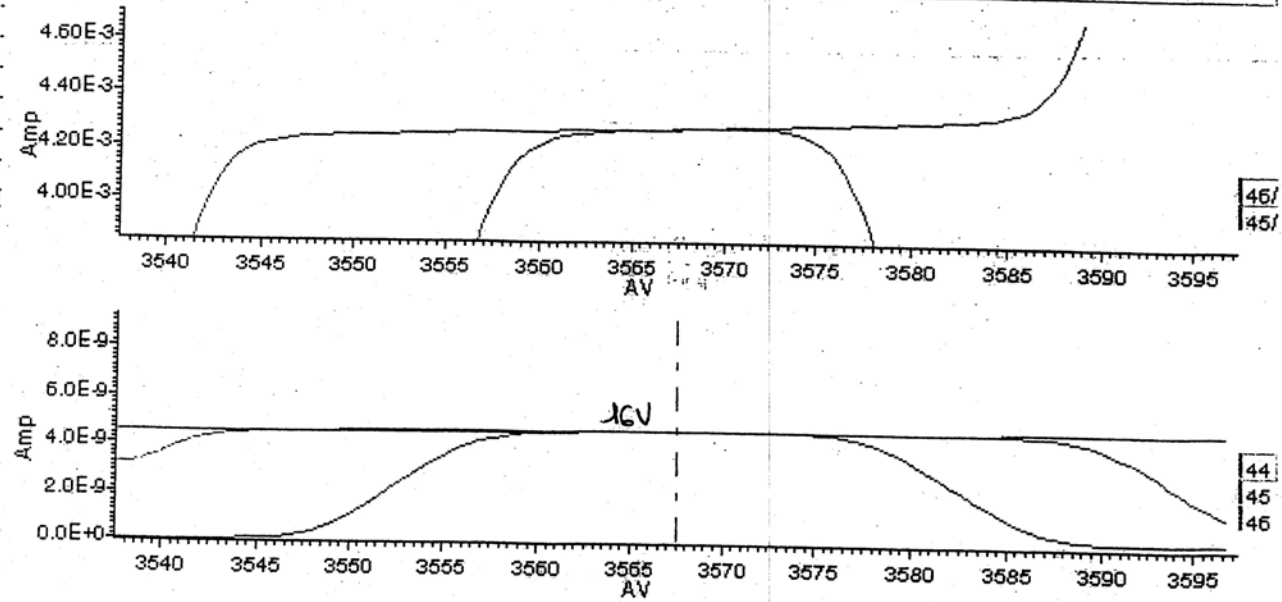
*Cet enregistrement est à transmettre au responsable du secteur confirmation concerné  
puis à archiver vivant dans le dossier matériel de l'appareil concerné dans la section correspondante.*

Optima GC 1.67-2

Inlet Mass Spec Scan Tests Analysis User Program Config Help

Current Mass: 45.00 Date: 23/07/06 Time: 09:26:57  
Mass-44 = 4.6584E-9 A  
Mass-45 = 5.4856E-11 A  
Mass-46 = 1.9935E-11 A  
FID = 0.09410 V  
Slice status = 0  
Penning = 5.2E-6 mBar  
Piran = 1.4E-2 mBar  
Turbo speed = 1.0E+2 mBar

Scan Display Window  
Graph Cursor Lines Window Scan





Data Processing Results

Data File Name : DATA\_003  
 Folder : 230706  
 Sample Name : stabilite 3  
 Sample ID :  
 Sample Position : 3  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : CO2-STAB  
 Batch Name : 230706  
 RunTime User : micromass  
 Acquisition Time : 09:50:48 Date : 23/07/06  
 Current Time : 10:01:52 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.5	8.459E-8	1.1780E-2	4.2498E-3
102.5	8.466E-8	1.1780E-2	4.2496E-3
162.5	8.456E-8	1.1780E-2	4.2494E-3
222.6	8.442E-8	1.1780E-2	4.2494E-3
282.6	8.499E-8	1.1779E-2	4.2495E-3
342.6	8.562E-8	1.1779E-2	4.2498E-3
402.6	8.627E-8	1.1779E-2	4.2500E-3
462.7	8.632E-8	1.1780E-2	4.2503E-3
522.7	8.640E-8	1.1780E-2	4.2506E-3
582.7	8.618E-8	1.1780E-2	4.2511E-3

Std Dev Of Fit 5.2114E-7 3.2526E-7

Analysis of Sample Peaks, with Zero Subtraction

CO2  
 Time Height Area 2/1 3/1 dC13Pk dO18Pk

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Data Processing Results

Data File Name : DATA 004  
 Folder : 230706  
 Sample Name : Mix cal IRMS 003-1  
 Sample ID :  
 Sample Position : 1  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-38  
 Batch Name : 230706  
 RunTime User : micromass  
 Acquisition Time : 10:01:53 Date : 23/07/06  
 Current Time : 10:17:37 Date : 23/07/06

Analysis of Reference Gas Data  
 Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.6	8.584E-8	1.1782E-2	4.2517E-3
102.5	8.610E-8	1.1781E-2	4.2518E-3
742.8	8.466E-8	1.1781E-2	4.2505E-3
802.8	8.551E-8	1.1780E-2	4.2508E-3

Std Dev Of Fit 1.4024E-7 2.0412E-7

Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
190.1	5.97E-9	1.5080E-8	1.1797E-2	4.1720E-3	-32.52	-37.68
255.7	4.55E-9	1.5439E-8	1.1844E-2	4.1833E-3	-28.45	-35.04
347.0	4.99E-9	1.5465E-8	1.1803E-2	4.1717E-3	-31.96	-37.68
533.3	4.58E-9	1.4792E-8	1.1806E-2	4.1565E-3	-31.51	-41.13

Data Processing Results

Data File Name : DATA\_005  
 Folder : 230706  
 Sample Name : Mix cal IRMS 003-2  
 Sample ID :  
 Sample Position : 1  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-38  
 Batch Name : 230706  
 RunTime User : micromass  
 Acquisition Time : 10:17:39 Date : 23/07/06  
 Current Time : 10:48:38 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.6	8.531E-8	1.1780E-2	4.2517E-3
102.6	8.503E-8	1.1781E-2	4.2516E-3
742.8	8.519E-8	1.1781E-2	4.2515E-3
802.9	8.535E-8	1.1781E-2	4.2517E-3

Std Dev Of Fit 1.1951E-7 1.2352E-7

Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
190.1	4.41E-9	1.0634E-8	1.1793E-2	4.1708E-3	-32.74	-37.95
256.0	3.29E-9	9.8960E-9	1.1845E-2	4.1762E-3	-28.28	-36.73
346.7	3.56E-9	1.0850E-8	1.1801E-2	4.1747E-3	-32.13	-37.07
532.7	2.94E-9	9.9025E-9	1.1804E-2	4.1652E-3	-31.76	-39.26

Data Processing Results

Data File Name : DATA\_006  
 Folder : 230706  
 Sample Name : Mix cal IRMS 003-3  
 Sample ID :  
 Sample Position : 1  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-38  
 Batch Name : 230706  
 RunTime User : micromass  
 Acquisition Time : 10:33:24 Date : 23/07/06  
 Current Time : 10:49:07 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.6	8.547E-8	1.1781E-2	4.2518E-3
102.5	8.560E-8	1.1781E-2	4.2520E-3
742.8	8.464E-8	1.1781E-2	4.2511E-3
802.9	8.481E-8	1.1780E-2	4.2510E-3

Std Dev Of Fit 4.0299E-7 1.5020E-7

Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
190.1	5.78E-9	1.4231E-8	1.1796E-2	4.1698E-3	-32.56	-38.23
255.2	4.35E-9	1.4943E-8	1.1842E-2	4.1838E-3	-28.65	-34.98
346.5	4.74E-9	1.4336E-8	1.1803E-2	4.1712E-3	-31.95	-37.86
533.2	4.26E-9	1.3575E-8	1.1806E-2	4.1602E-3	-31.59	-40.36

Data Processing Results

Data File Name : DATA\_007  
 Folder : 230706  
 Sample Name : Mix cal Acetate 001A-100ng inj  
 Sample ID :  
 Sample Position : 2  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 10:53:36 Date : 23/07/06  
 Current Time : 11:39:17 Date : 23/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.5	8.609E-8	1.1781E-2	4.2521E-3
182.6	8.616E-8	1.1781E-2	4.2522E-3
242.6	8.618E-8	1.1781E-2	4.2523E-3
2423.4	8.509E-8	1.1781E-2	4.2519E-3
2483.5	8.465E-8	1.1781E-2	4.2516E-3
2533.4	8.528E-8	1.1780E-2	4.2520E-3

Std Dev Of Fit 1.7125E-7 1.7134E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	866.6	4.79E-9	2.0679E-8	1.1821E-2	4.1654E-3	-30.29	-68.47	-39.32	24
	1229.8	4.79E-9	3.7785E-8	1.1938E-2	4.1666E-3	-20.01	-66.70	-39.05	24
	1302.2	3.63E-9	2.8202E-8	1.1782E-2	4.1663E-3	-33.70	-66.54	-39.08	24
	1473.8	3.17E-9	3.2254E-8	1.1976E-2	4.1665E-3	-16.69	-66.30	-39.06	24

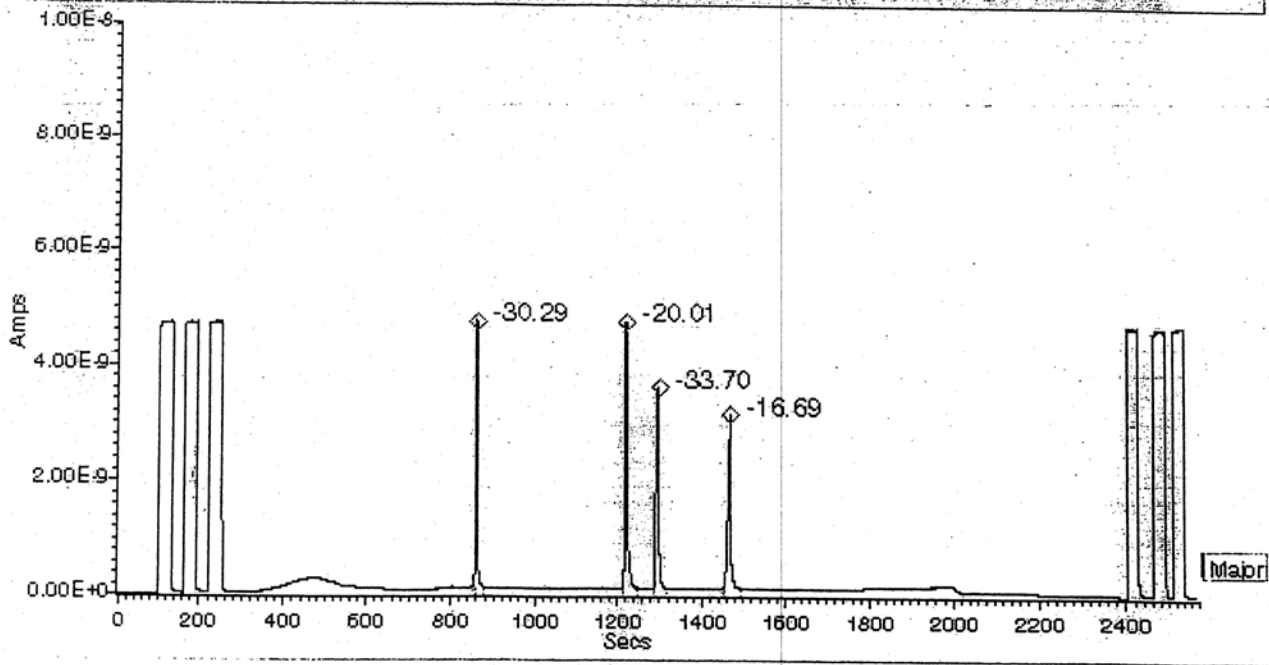
DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_007      Folder : 230706  
            Date : 23/07/06      Time : 10:53:36  
            Comment : Mix cal Acetate.001A-100ng.inj  
Parameters      Automatic DP Params

Data Processing Main Graph

Graph Cursor Lines Window



Data Processing Results

Data File Name : DATA\_014  
 Folder : 230706  
 Sample Name : Mix Cal Acetate 001A-2  
 Sample ID :  
 Sample Position : 2  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name : 230706  
 RunTime User : micromass  
 Acquisition Time : 20:39:04 Date : 23/07/06  
 Current Time : 14:24:44 Date : 24/07/06

Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.663E-8	1.1777E-2	4.2533E-3
182.6	8.686E-8	1.1778E-2	4.2533E-3
242.6	8.696E-8	1.1777E-2	4.2538E-3
2423.5	8.634E-8	1.1776E-2	4.2523E-3
2483.5	8.613E-8	1.1776E-2	4.2525E-3
2533.4	8.650E-8	1.1776E-2	4.2530E-3

Std Dev Of Fit 2.3526E-7 3.3647E-7

Analysis of Sample Peaks, with Background Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
866.6	4.03E-9	1.7744E-8	1.1814E-2	4.1663E-3	-30.56	-69.16	-39.38	24
1228.5	4.07E-9	2.9964E-8	1.1932E-2	4.1684E-3	-20.22	-65.52	-38.89	24
1301.0	3.09E-9	2.3587E-8	1.1776E-2	4.1712E-3	-33.90	-65.65	-38.19	24
1471.6	2.60E-9	2.6828E-8	1.1972E-2	4.1715E-3	-16.76	-67.09	-38.15	24

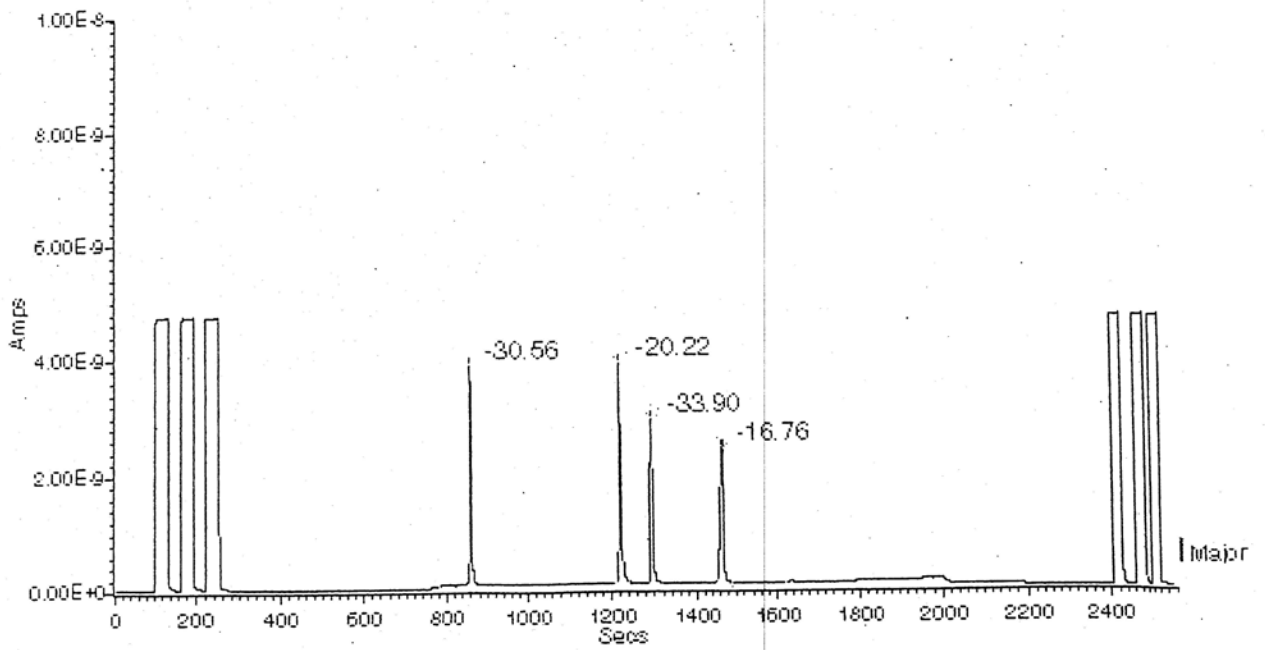
Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_014      Folder : 230706  
            Date : 23/07/06      Time : 20:39:04  
            Comment : Mix Cal Acetate 001A-2 : 230706  
Parameters      Automatic DP Params

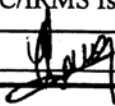
Data Processing Main Graph

Graph Cursor Lines Window





<b>LNDD</b>	<b>ENREGISTREMENT</b>	Codification : E-FCR-06 Version : E Date : 24/11/05 Page : 1/2
<b>FICHE D'ANALYSE / RESULTATS GC/C/IRMS</b>		

Echantillon :  Instrument :   
 Répertoire :  CO et paraphe :    
 Valeur isotopique du réactif de dérivation :

**Fraction F1 (métabolites de la cortisone et du cortisol)**

	Blanc urinaire		Echantillon	
	SI	11 Kétoétio	SI	11 Kétoétio
Nom du fichier	Data_010	Data_010	Data_011	Data_011
tr (s)	867	1474	867	1478
trr	-	1.700	-	1.705
Intensité (nA)	3.7	3.3	4.0	4.6
$\delta^{13}\text{C}$ ‰ mesurée	-30.80	-24.55	-31.64	-24.10
$\delta^{13}\text{C}$ ‰ corrigée	-	-21.56	-	-21.06

**Fraction F2 (Kétos)**

	Blanc urinaire			Echantillon		
	SI	Etio	Andro	SI	Etio	Andro
Nom du fichier	Data_012	Data_012	Data_012	Data_013	Data_013	Data_013
tr (s)	868	1232	1257	866	1230	1254
trr	-	1.419	1.448	-	1.420	1.448
Intensité (nA)	2.7	4.5	5.3	2.2	4.0	3.4
$\delta^{13}\text{C}$ ‰ mesurée	-29.94	-25.34	-24.98	-30.07	-26.43	-27.71
$\delta^{13}\text{C}$ ‰ corrigée	-	-22.43	-22.03	-	-23.63	-25.05

**Fraction F3 (Diols)**

	Blanc urinaire			
	SI	5 $\beta$ Adiol	5 $\alpha$ Adiol	5 $\beta$ Pdiol
Nom du fichier	Data_008	Data_008	Data_008	Data_008
tr (s)	867	1306	1337	1652
trr	-	1.506	1.541	1.904
Intensité (nA)	6.2	7.1	2.3	3.6
$\delta^{13}\text{C}$ ‰ mesurée	-30.66	-27.54	-28.40	-26.65
$\delta^{13}\text{C}$ ‰ corrigée	-	-22.18	-23.22	-21.63

	Echantillon			
	SI	5 $\beta$ Adiol	5 $\alpha$ Adiol	5 $\beta$ Pdiol
Nom du fichier	Data_009	Data_009	Data_009	Data_009
tr (s)	867	1305	1337	1652
trr	-	1.504	1.542	1.905
Intensité (nA)	6.8	5.5	2.6	3.3
$\delta^{13}\text{C}$ ‰ mesurée	-30.05	-28.82	-32.12	-26.61
$\delta^{13}\text{C}$ ‰ corrigée	-	-23.73	-27.72	-21.58

<b>LNDD</b>	<b>ENREGISTREMENT</b>	Codification : <b>E-FCR-06</b>
		Version : E
		Date : 24/11/05
		Page : 2/2
<b>FICHE D'ANALYSE / RESULTATS GC/C/IRMS</b>		

	valeur de référence d'une population témoin		Echantillon dans les normes	
	$\delta^{13}\text{C} \text{‰}$ haute	$\delta^{13}\text{C} \text{‰}$ basse	oui	non
11 Kétoétio	-17.58	-26.27	✗	
Etio	-19.56	-26.10	✗	
Andro	-18.43	-25.02		✗
5 $\beta$ Adiol	-18.55	-26.97	✗	
5 $\alpha$ Adiol	-18.59	-27.40		✗
5 $\beta$ Pdiol	-18.25	-25.55	✗	

	Blu	Echantillon		
	$\Delta \text{‰}$	$\Delta \text{‰} + 0,8 \text{‰}$	$\Delta \text{‰}$	$\Delta \text{‰} - 0,8 \text{‰}$
Etio - 11 Kétoétio	-0.87	-1.78	-2.58	-3.38
Andro - 11 Kétoétio	-0.48	-3.19	-3.99	-4.79
5 $\beta$ Adiol - 5 $\beta$ Pdiol	-0.55	-1.35	-2.15	-2.95
5 $\alpha$ Adiol - 5 $\beta$ Pdiol	-1.59	-5.34	-6.14	-6.94

Seuil de positivité de l'AMA:  $\delta^{13}\text{C} \text{‰}(\text{métabolite}) - \delta^{13}\text{C} \text{‰}(\text{composé endogène de référence}) > 3 \text{‰}$   
 $\delta^{13}\text{C}$  du composé  $< -28 \text{‰}$ .

Variation maximale admissible liée à la méthode: +/- 0,8‰

### Conclusion

L'analyse de l'échantillon par spectrométrie de masse de rapport isotopique (EC31) indique une origine exogène des métabolites de la testostérone, cohérente avec une prise de testostérone ou de l'un de ses précurseurs.

L'origine exogène des métabolites de la testostérone a été objectivée sur la base d'un appauvrissement isotopique de 3.99‰ et 6.14‰, respectivement pour les métabolites androstérone et 5 $\alpha$  androstanediol.

*Partie à remplir par le responsable*

Paraphe du responsable:

*CB*

Observations:

USADA 0186

Ecart(s) n° :

*Cet enregistrement est à mettre dans le dossier de confirmation*

*175*