

Impinger Studies of Volatility of FC-95 and FC-143

Intoduction and Purpose :

Thermospray mass spectrometry was used to quantitate a number of samples for FC-143 and FC-95. The overall purpose of this experiment is to determine whether or not FC-95 and/or FC-143 has an appreciable vapor pressure at room temperature. This experiment consists of two parts. The first part of this experiment is to test whether either of these compounds are removed from a variety of solutions when air is bubbled through them. In the second part of this experiment, a solution of ammonium acetate in 1-propanol:water is used to trap any FC-95 and/or FC-143 that volatilizes at room temperature.

Part I

The solutions that were tested to see if either or both of the fluorochemicals are removed from them upon passing air through them are described below:

Label	Compound	Concentration	[FC95]	[FC143]
1	Tetrabutylammonium hydroxide	500 ppm	10.0 ppm	10.0 ppm
2	Ammonium acetate	500	10.0	10.0
3	Laurylpyridinium chloride	503	10.0	10.0
4	n-Alkyldimethylbenzylammonium chloride	500	10.0	10.0
5	Cetyltrimethylammonium bromide	500	10.0	10.0
6	Tallowtrimethylammonium chloride	505	10.0	10.0
7	Dicocodimethylammonium chloride	500	10.0	10.0
8	Water/1-propanol (50:50)	0	10.0	10.0
9	Water/1-propanol (50:50)	0	0.00	0.00
100A	Amonium acetate in water/1-propanol (50:50)	500	0.10	0.10
200A	Amonium acetate in water/1-propanol (50:50)	500	0.20	0.20
400A	Amonium acetate in water/1-propanol (50:50)	500	0.40	0.40
800A	Amonium acetate in water/1-propanol (50:50)	500	0.80	0.80
2000A	Amonium acetate in water/1-propanol (50:50)	500	2.00	2.00

Part II

A 50:50 water/1-isopropanol solution containing 500 ppm ammonium acetate was used in the second part of this experiment. In this part of the experiment, FC-95 or FC-143 is placed in an apperatus which air is passed through. Glass wool is placed downwind of the fluorochemicals to trap any particulates. After the air passes over the fluorochemicals and through the glass wool, it is bubbled through a train of impingers containing the ammonium acetate solution. If the first part of the experiment shows that there is no loss of fluorochemicals upon passing air through the solutions, it is expected that if there is any fluorochemicals present in the air, they will be transferred to and retained by the ammonium acetate solution.

Experimental

An Extrel ELQ-400 was used with a Vestec thermospray to quantitate these samples. FC-95 is quantified by monitoring the ion current at m/z 499, FC-143 is quantified by monitoring the ion current at m/z 413. A Waters 600-MS HPLC pump with SILK was used with a Waters WISP 712 autoinjector for delivering 10 μ L injections of the sample to the thermospray. The mobile phase composition was 39:60:1 acetonitrile:water:1 ppm tetrabutylammonium chloride flowed at 1.5 ml/min. The tip temp pot was set to 4.75 while the block pot was set to 5.3.

For each sample, three injections were made for both the stock solutions, which were spiked with the fluorochemicals but did not have air blown through them, and the "blow" solutions, which are identical to the stock solutions except that they had 280 liters of air passed through them. Thus, the stock solutions serve as controls for measuring loss of fluorochemicals. The stock and blow solution injections were staggered to minimize the effects of any drift in the mass spec response. The integrated areas of the selected ion currents for the blow and stock solutions are averaged, adjusted for volume changes caused by passing the air through the impinger, and then ratioed. This adjusted ratio then reflects the amount of fluorochemical that remained in solution after passing the air through the impinger. A ratio of 1.00 indicates no loss of fluorochemicals, while a ratio of 0.00 would indicate a total loss of the fluorochemicals upon passing air through the solution.

Results

Part I

The results of Part I of this experiment are summarized below. These results indicate that there is some loss of fluorochemicals upon passing air through most of the solutions, but most of the solutions retained 85% or more of both fluorochemicals. This suggests that both FC95 and FC143 are capable of volatilizing out of most of these solutions.

Solution	% Retained - FC143	% Retained - FC95
Tetrabutylammonium hydroxide	83	90
Ammonium acetate	90	71
Laurylpyridinium chloride	90	90
n-Alkyldimethylbenzylammonium chloride	101	100
Cetyltrimethylammonium chloride	95	95
Tallowtrimethylammonium chloride	90	93
Dicocodimethylammonium chloride	89	84
Water/1-Propanol (50:50)	85	89
Ammonium acetate in water/1-propanol (50:50) 100 ppb	98	96
Ammonium acetate in water/1-propanol (50:50) 200 ppb	108	101
Ammonium acetate in water/1-propanol (50:50) 400 ppb	85	90
Ammonium acetate in water/1-propanol (50:50) 800 ppb	89	95
Ammonium acetate in water/1-propanol (50:50) 2000 ppb	92	96

Part II

No fluorochemicals were found to be present in either the first or second impinger. This indicates that the amounts of FC95 and FC143 transported from the solids to air and then into the solution is below the sensitivity of the instrument, thus suggesting that both compounds are involatile or have very low vapor pressures as solids.

Part II

No fluorochemicals were found to be present in either the first or second impinger. This indicates that the amounts of FC95 and FC143 transported from the solids to air and then into the solution is below the sensitivity of the method, thus suggesting that both compounds are involatile or have very low vapor pressures as solids at room temperature. Estimates of the maximum vapor pressure of these compounds are presented below.

Conclusions

Almost all of the solutions tested in the first part of the experiment retained over 80% of both fluorochemicals, with an average retention of 92 % for both FC95 and FC143. This indicates that there is loss of the fluorochemicals from most of the solutions, but some of the solutions, particularly the n-alkyldimethylbenzylammonium chloride solution, appears to retain all of the fluorochemicals.

A solution of 500 ppm ammonium acetate in a 50:50 mixture of water:1-propanol was used in the second part of this experiment. The solutions of ammonium acetate in water:1-propanol had an average percent retention of 94% for FC95 and 93% for FC143.

Neither PFO nor PFOS was found in any of the impingers that were tested in the second part of this experiment. The sensitivity of the method is such that the fluorochemicals should be detected in the impingers if the vapor pressure of the given compound exceeds approximately $1 \cdot 10^{-7}$ torr. Since neither compound was observed, the vapor pressure of both of these compounds is less than $1 \cdot 10^{-7}$ torr.

This experiment does not address issues related to kinetics of phase transfer, which may be important.

Maximum Vapor Pressure Calculations

Minimum concentration required to quantify using thermospray mass spec : 25 ppb

Minimum amount of fluorochemical transferred to impinger needed to quantify :

$$(.025 \text{ ug / ml})(25 \text{ ml}) = 0.625 \text{ ug / ml} \quad \text{Eq. 1}$$

Assuming that 90% of the fluorochemicals that are transferred to the air will be trapped by the first impinger, the minimum amount of fluorochemical that needs to be present in the 280 liters of air that is passed over the fluorochemical and through the impinger train:

$$(0.625 \text{ ug / ml}) / 0.9 = 0.7 \text{ ug} \quad \text{Eq. 2}$$

Converting this to moles of FC95 and FC143 gas molecules:

FC95

$$\frac{0.7 \cdot 10^{-6} \text{ g}}{538 \text{ g / mol}} = 1.3 \cdot 10^{-9} \text{ mol} \quad \text{Eq. 3}$$

FC143

$$\frac{0.7 \cdot 10^{-6} \text{ g}}{431 \text{ g / mol}} = 1.6 \cdot 10^{-9} \text{ mol} \quad \text{Eq. 4}$$

Assuming the air behaves as a mixture of ideal gases and the air is at standard pressure, the number of moles of air molecules in 280 liters of air at 20 °C is:

$$\frac{280 \text{ liters} \cdot 273 \text{ K}}{(22.414 \text{ liters / mol}) \cdot 293 \text{ K}} = 11.4 \text{ mol} \quad \text{Eq. 5}$$

The following equation then gives the minimum vapor pressure the fluorochemical salts must have to be measured by this experiment :

FC95

$$\frac{1.3 \cdot 10^{-9} \text{ mol}}{11.4 \text{ mol}} \cdot 760 \text{ torr} = 8.7 \cdot 10^{-8} \text{ torr} \quad \text{Eq. 6}$$

FC143

$$\frac{1.6 \cdot 10^{-9} \text{ mol}}{11.4 \text{ mol}} \cdot 760 \text{ torr} = 1.1 \cdot 10^{-7} \text{ torr} \quad \text{Eq. 7}$$

Since no fluorochemicals were found in any of the impingers that were tested, the vapor pressures of these two compounds is less than the minimum values shown in equations 6 and 7.

Part I Data

PFOs

Sample	1st Inject	2nd Inject	3rd Inject	Average	% (Aerated/Stock)	% Retained
1-Stock	3503	3968	4421	3964		
1-Aerated	4074	4444	4254	4257	107	90
2-Stock	4184	4361	3254	3933		
2-Aerated	4026	3388	3590	3668	93	71
3-Stock	2576	2598	2583	2586		
3-Aerated	2614	2699	2785	2699	104	90
4-Stock	3890	4120	4250	4087		
4-Aerated	4243	4426	4595	4421	108	100
5-Stock	2443	2454	2427	2441		
5-Aerated	2516	2542	2502	2520	103	95
6-Stock	5779	5778	6080	5879		
6-Aerated	6219	6589	6635	6481	110	93
7-Stock	5436	6031	6175	5881		
7-Aerated	5778	5964	5156	5633	96	84
8-Stock	6155	6338	5539	6011		
8-Aerated	6583	7342	5246	6390	106	89
9-Stock	0	0	0			
9-Aerated	0	0	0			
					% Retained	± /100 A
100 A	134	93	99	109		
100 B	140	109	108	119	96	96
200 A	175	185	188	183		168
200 B	209	210	208	209	101	169
400 A	317	316	363	332		306
400 B	391	382	353	375	90	276
800 A	563	568	471	534		491
800 B	615	633	411	553	95	468
2000 A	1303	1286	815	1135		1044
2000 B	1389	1331	981	1234	96	999

Part I Data

PFO

Sample	1st Inject	2nd Inject	3rd Inject	Average	%Blow/Stock	Adjusted %
1-Stock	2963	3157	3434	3185		
1-Blow	2989	3407	3067	3154	99	83
2-Stock	3334	3247	2093	2891		
2-Blow	3702	2533	2621	2952	102	90
3-Stock	3033	3197	3674	3301		
3-Blow	3207	3471	3631	3436	104	90
4-Stock	4751	5466	5877	5365		
4-Blow	5522	5854	6294	5890	110	101
5-Stock	3884	4612	4444	4313		
5-Blow	4273	4342	4798	4471	104	95
6-Stock	4052	4107	4207	4122		
6-Blow	4361	4371	4540	4424	107	90
7-Stock	3811	3625	3586	3674		
7-Blow	3838	3768	3500	3702	101	89
8-Stock	5076	5181	5105	5121		
8-Blow	5220	5390	5008	5206	102	85
9-Stock	0	0	0			
9-Blow	0	0	0			
					% B/A	% /100 A
100 A	105	81	88	91		
100 B	125	89	90	101	98	98
200 A	136	164	129	143		157
200 B	181	163	181	175	108	169
400 A	295	274	311	293		321
400 B	316	326	292	311	85	273
800 A	515	532	365	471		515
800 B	530	537	301	456	89	459
2000 A	1201	1196	590	996		1090
2000 B	1226	1182	712	1040	92	1002

Part II Data

PFO

Sample	1st Inject	2nd Inject	3rd Inject	Average
T1 I1	0	0	0	0
T1 I2	0	0	0	0
T2 I1	0	0	0	0
T2 I2	0	0	0	0
T2 I1	0	0	0	0
T2 I2	0	0	0	0

PFOS

Sample	1st Inject	2nd Inject	3rd Inject	Average
T1 I1	0	0	0	0
T1 I2	0	0	0	0
T2 I1	0	0	0	0
T2 I2	0	0	0	0
T3 I1	0	0	0	0
T3 I2	0	0	0	0

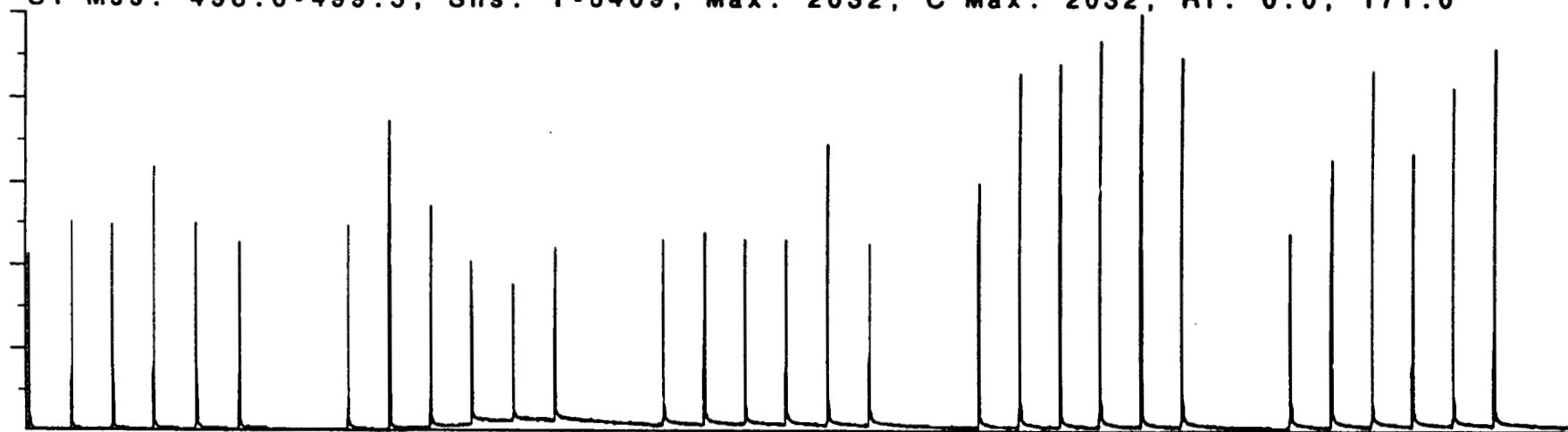
[illegible]

SAMPLE DESCRIPTION	IMPINGER SOLUTION	INITIAL VOLUME (mls)	FINAL VOLUME (mls)	START TIME	END TIME	SAMPLE PERIOD (minutes)	FLOW RATE (liters/min)	TOTAL AIR VOLUME (liters)
Train 1 / Impinger 1	H2O / 1-Propanol 500 ppm Ammonium Acetate	25		10:45	Auto	280	1	280
Train 1 / Impinger 2	H2O / 1-Propanol 500 ppm Ammonium Acetate	25		10:45	Auto	280	1	280
Train 2 / Impinger 1	H2O / 1-Propanol 500 ppm Ammonium Acetate	25		10:45	Auto	280	1	280
Train 2 / Impinger 2	H2O / 1-Propanol 500 ppm Ammonium Acetate	25		10:45	Auto	280	1	280
Train 3 / Impinger 1	H2O / 1-Propanol 500 ppm Ammonium Acetate	25		10:45	Auto	See Comment	1	See Comment
Train 3 / Impinger 2	H2O / 1-Propanol 500 ppm Ammonium Acetate	25		10:45	Auto	See Comment	1	See Comment

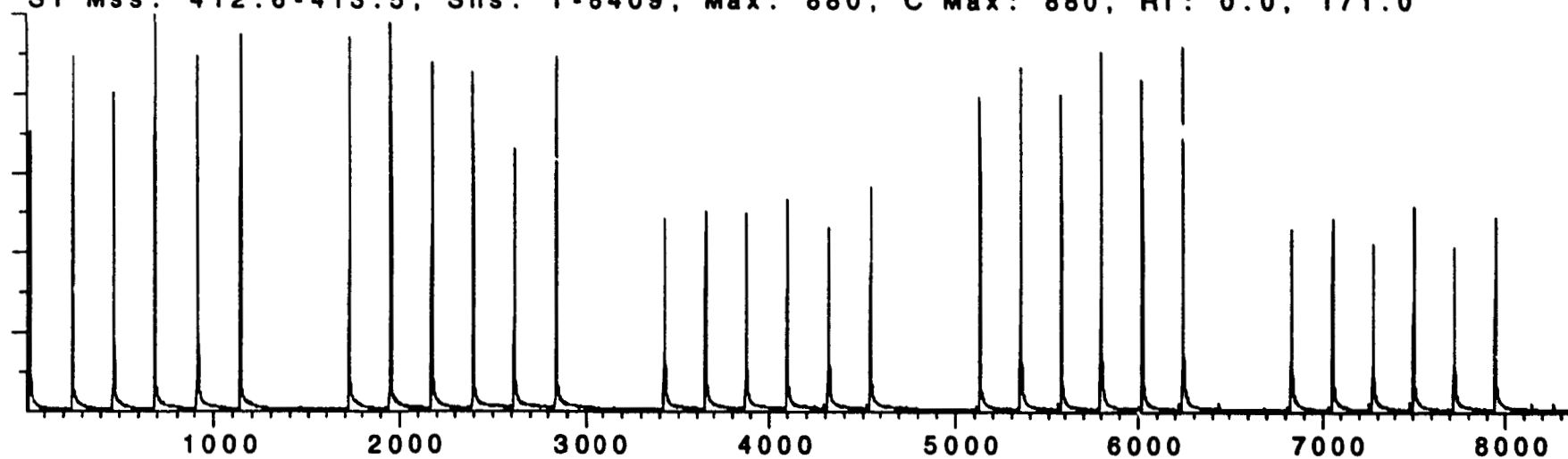
COMMENTS: Pump on Train 3 failed at 181 minutes. There was a 25 minute span of time when no sample was being pumped. The total sample time was 255 minutes.

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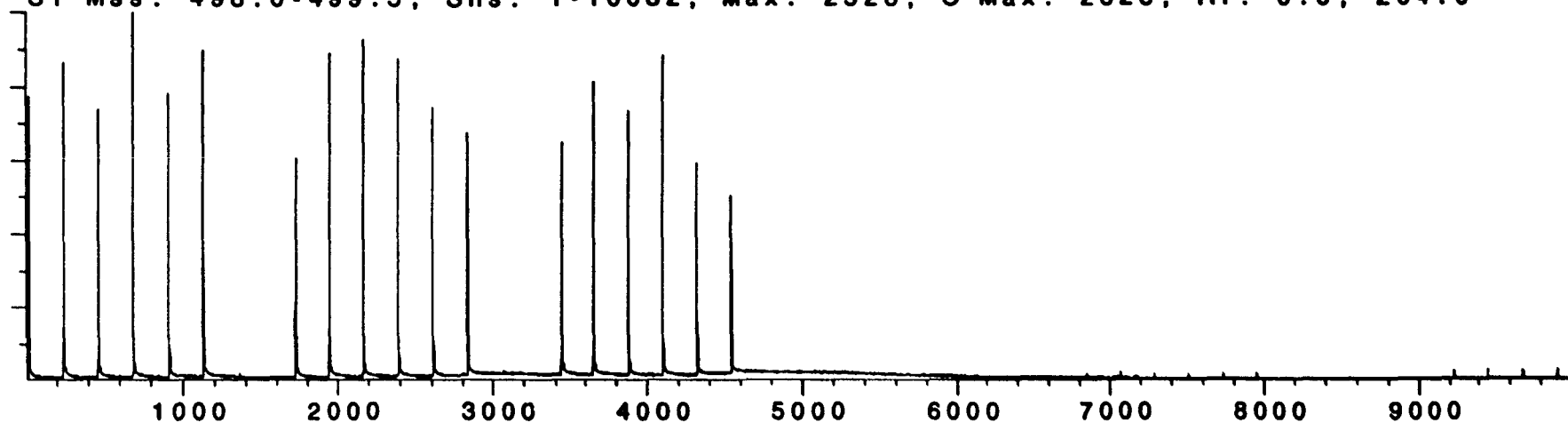


S1 Mss: 412.6-413.5, Sns: 1-8409, Max: 880, C Max: 880, RT: 0.0, 171.0



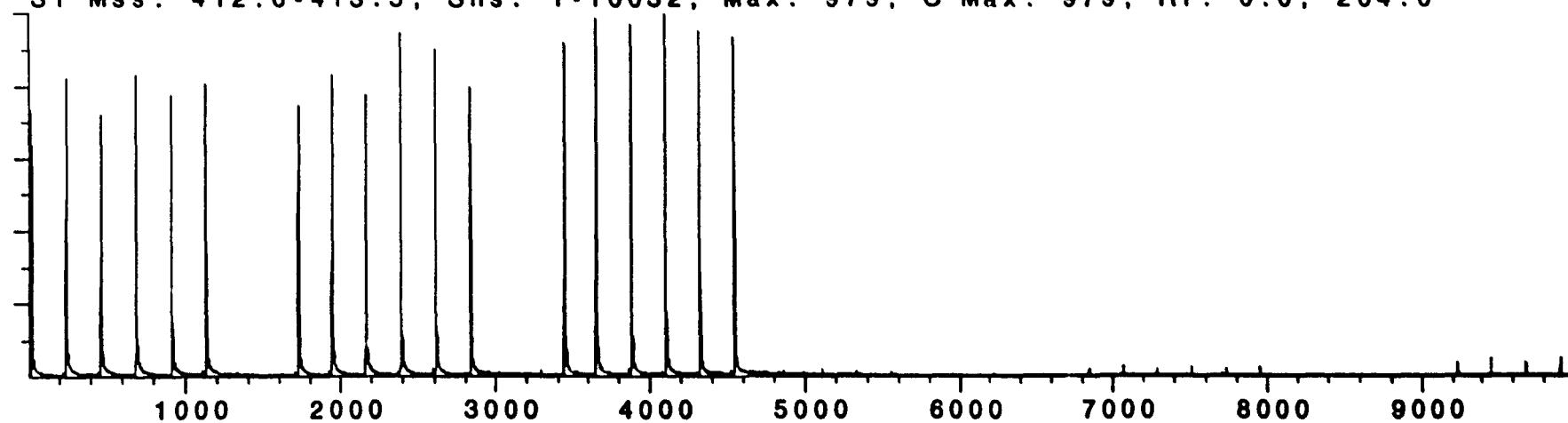
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S1 Mss: 498.6-499.5, Sns: 1-10032, Max: 2528, C Max: 2528, RT: 0.0, 204.0



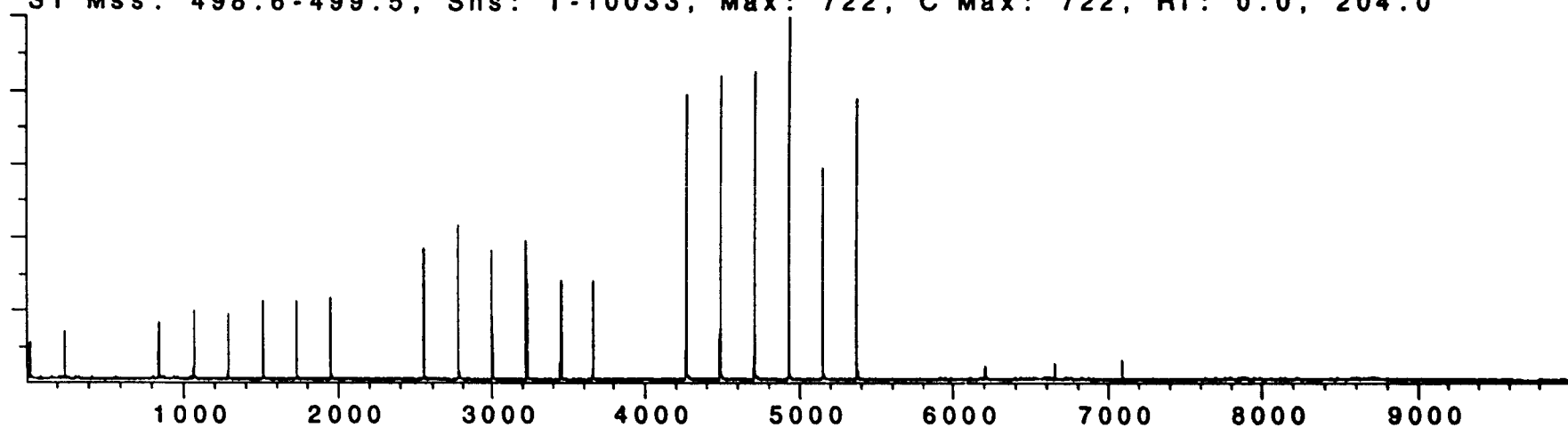
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S1 Mss: 412.6-413.5, Sns: 1-10032, Max: 979, C Max: 979, RT: 0.0, 204.0



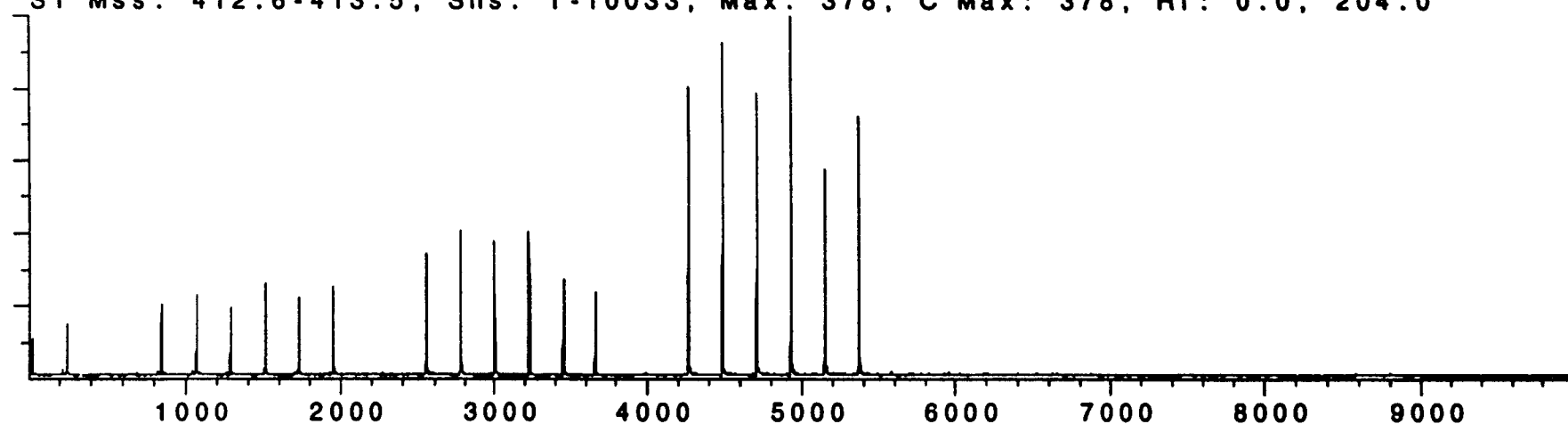
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S1 Mss: 498.6-499.5, Sns: 1-10033, Max: 722, C Max: 722, RT: 0.0, 204.0



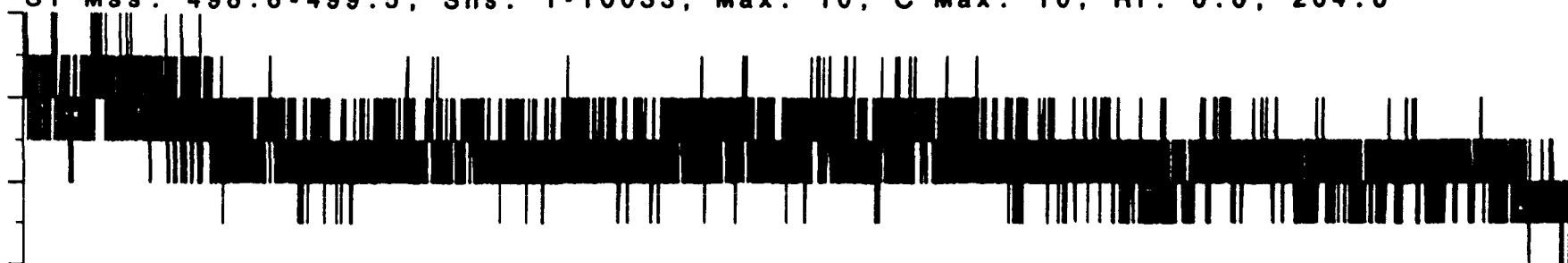
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S1 Mss: 412.6-413.5, Sns: 1-10033, Max: 378, C Max: 378, RT: 0.0, 204.0

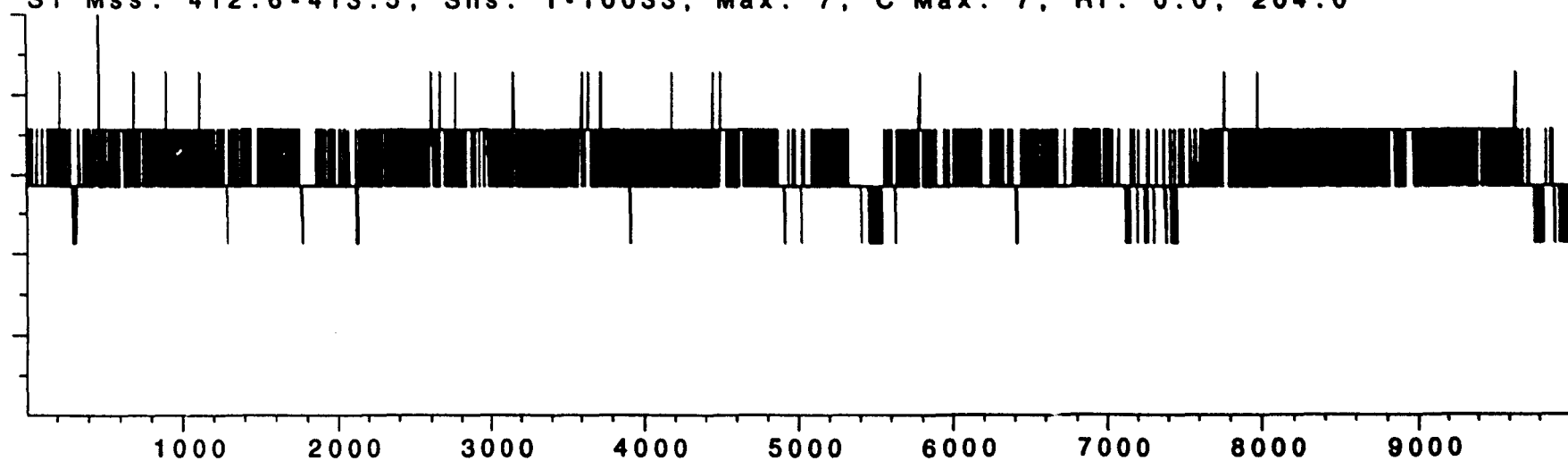


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S1 Mss: 498.6-499.5, Sns: 1-10033, Max: 10, C Max: 10, RT: 0.0, 204.0

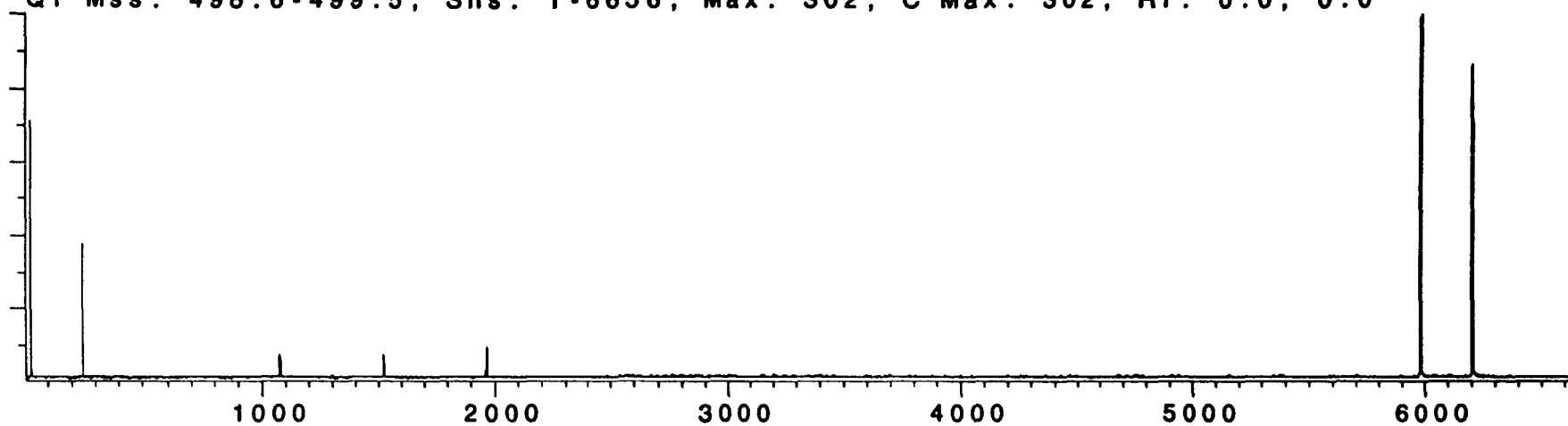


S1 Mss: 412.6-413.5, Sns: 1-10033, Max: 7, C Max: 7, RT: 0.0, 204.0



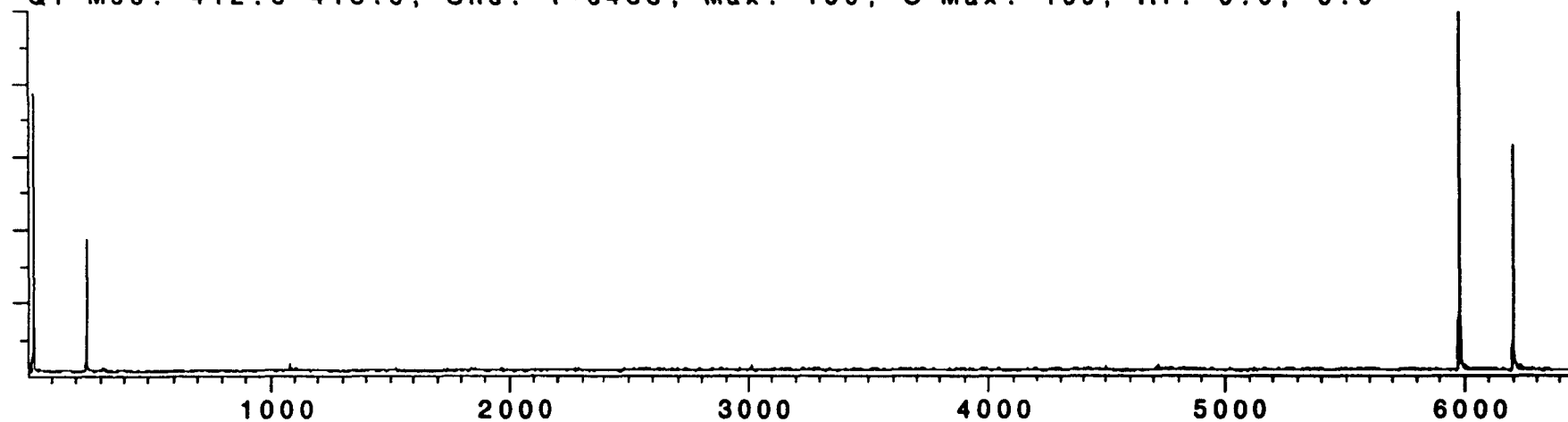
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Q1 Mss: 498.6-499.5, Sns: 1-6656, Max: 302, C Max: 302, RT: 0.0, 0.0



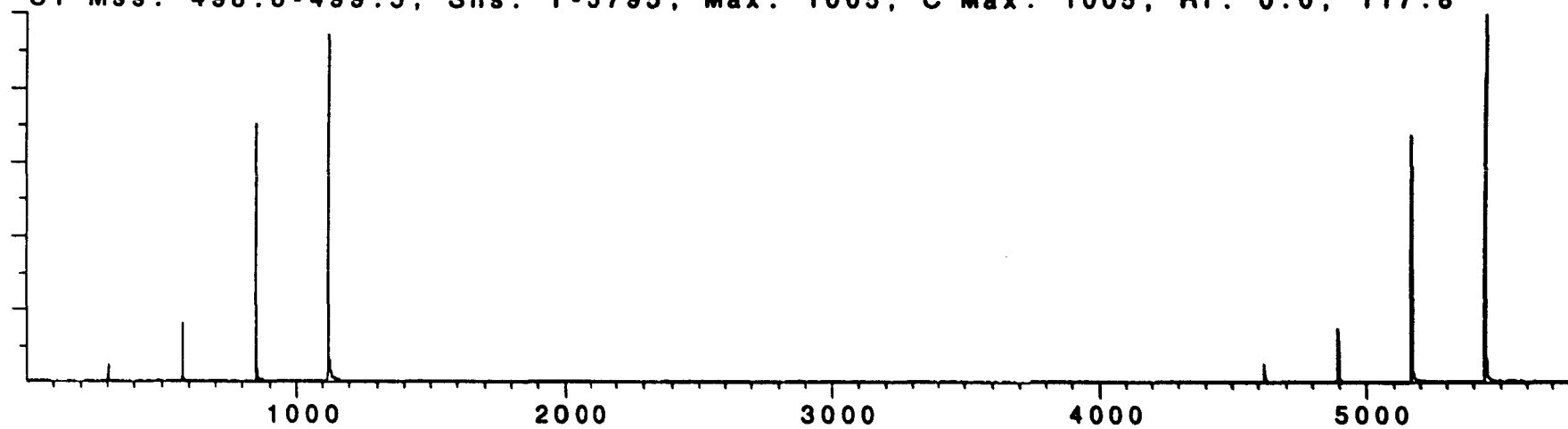
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Q1 Mss: 412.6-413.5, Sns: 1-6485, Max: 199, C Max: 199, RT: 0.0, 0.0



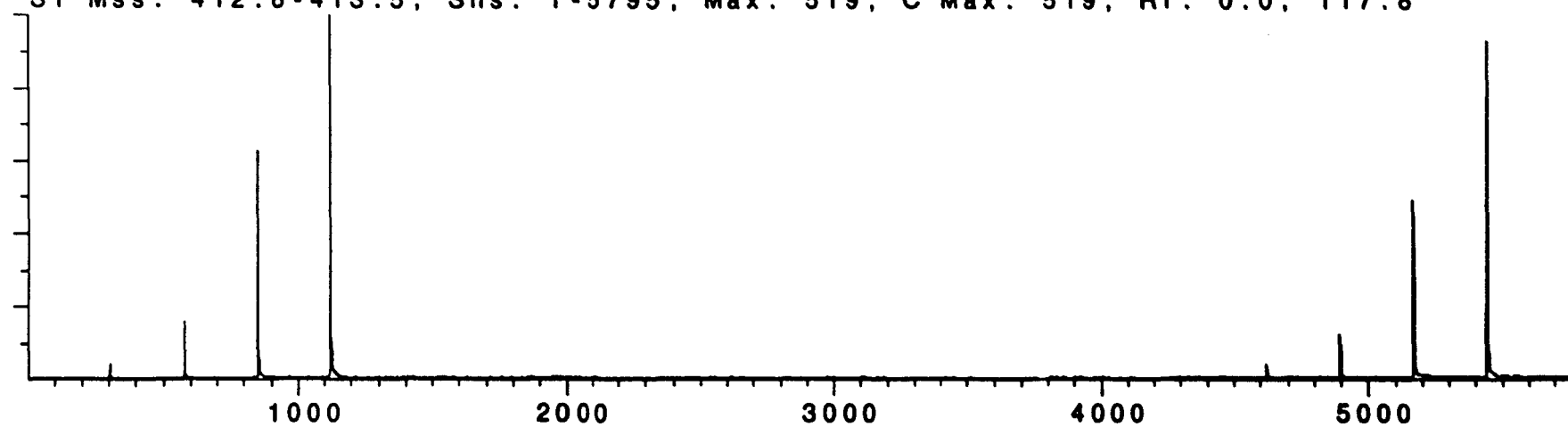
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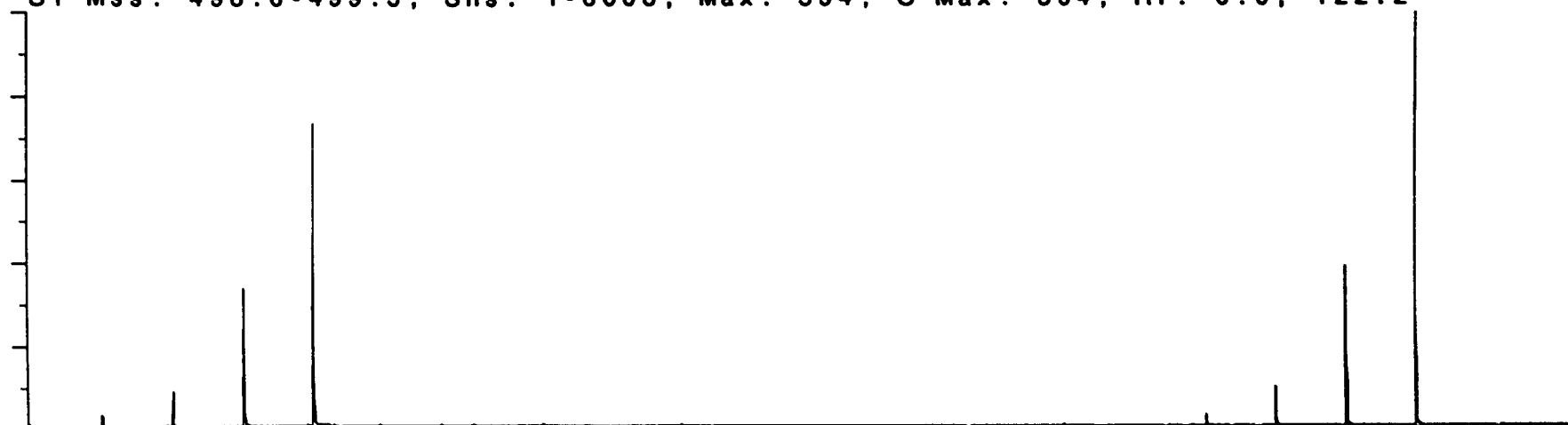
DU0:[301,1]D4726, , 08-OCT-93, 11:31:13

S1 Mss: 412.6-413.5, Sns: 1-5795, Max: 519, C Max: 519, RT: 0.0, 117.8

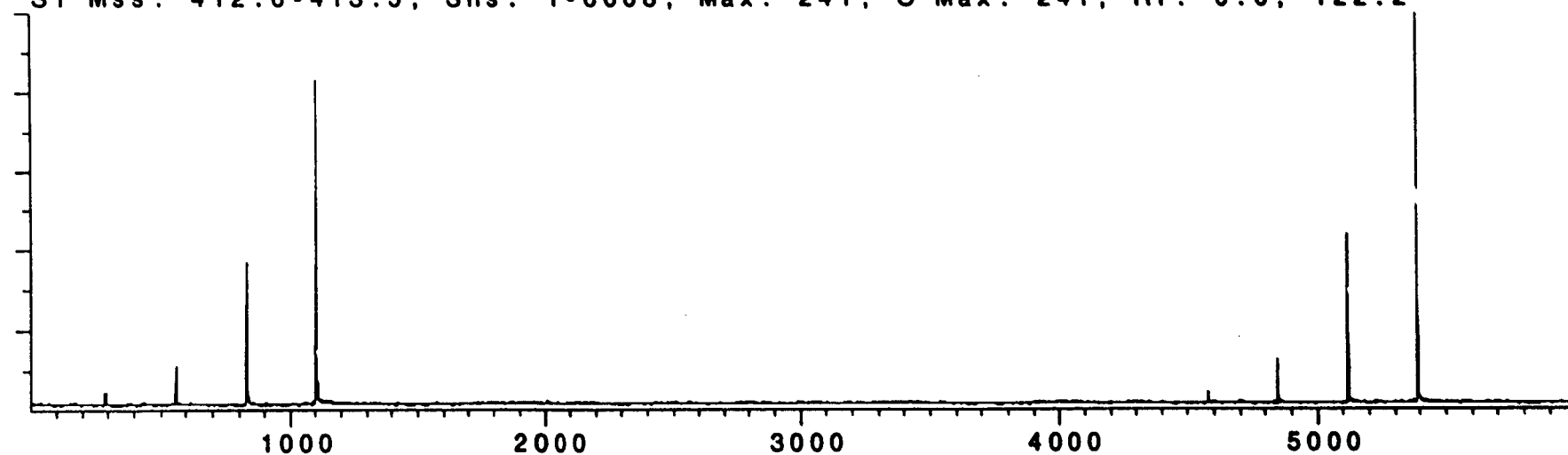


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S1 Mss: 498.6-499.5, Sns: 1-6008, Max: 594, C Max: 594, RT: 0.0, 122.2



S1 Mss: 412.6-413.5, Sns: 1-6008, Max: 241, C Max: 241, RT: 0.0, 122.2



Vapor Pressure Measurements of FC95 and FC143

Experiment #3

Introduction

This is a continuation of a series of experiments designed to obtain measurements of the vapor pressures of FC95 and FC143. This is the third experiment in this series. A second experiment was run prior to this experiment, but a solution was accidentally used in the impingers that had been spiked with 10 ppm FC95 and 10 ppm FC143. The intent of this experiment is to measure the vapor pressure of these two compounds at 90 C. The apparatus used in this experiment was described in a report entitled Impinger Studies of the Volatility of FC95 and FC143, which is filed in the LIRN system under L3306.

Results and Discussion

During this experiment, a 1-propanol:water (50:50) solution containing 500 ppm ammonium acetate was used in the impingers to catch any volatilized fluorochemicals. This solution was used to be consistent with the first experiment for measuring the vapor pressures of FC95 and FC143 at room temperature.

FC143 was found in all three impingers of both trains, indicating that FC143 has a measureable vapor pressure at 90 C. It also indicates that the solution used in the impinger trains is not efficient at catching fluorochemicals in the air that passes through them at the flow rates that were used in this experiment.

The vapor pressure of FC95 at 90 C measured much lower than the vapor pressure of FC143 in this experiment, but it does appear that FC95 has a measureable vapor pressure at this temperature. The amount of FC95 measured in the first impinger of both trains was higher than any of the reagent or impinger blanks. The values measured for the amounts of FC95 in the blank impingers were subtracted from the values measured for the amounts of FC95 in the impingers after the warm air had been bubbled through them before the vapor pressure calculations were performed.

The raw data and integrated data are shown in the following pages. The results of this experiment are given below. These results are minimum vapor pressures for the two compounds at 90 C, since it appears that the impinger trains did not catch all of the fluorochemicals that had been volatilized.

FC95	$1.2 \cdot 10^{-7}$ torr
FC143	$1.1 \cdot 10^{-5}$ torr

Vapor Pressure Calculations

Total amount of fluorochemicals found in the impinger trains :

FC95

Impinger train #1

$$(0.05 \cdot 15 + 0.02 \cdot 18 + 0.01 \cdot 7) = 1.2 \text{ ug}$$

Eq. 1A

$$0.75 \text{ ug} \quad 0.36 \text{ ug} \quad 0.07 \text{ ug}$$

Impinger train #2

$$(0.02 \cdot 9 + 0.02 \cdot 16 + 0.00 \cdot 8) = 0.5 \text{ ug}$$

Eq. 1B

$$0.18 \text{ ug} \quad 0.32 \text{ ug}$$

$$\text{Average} = 0.8 \text{ ug}$$

FC143

Impinger train #1

$$(1.43 \cdot 15 + 0.92 \cdot 18 + 2.34 \cdot 7) = 54.4 \text{ ug}$$

Eq. 2A

Impinger train #2

$$(0.95 \cdot 9 + 2.00 \cdot 16 + 1.91 \cdot 8) = 55.8 \text{ ug}$$

Eq. 2B

$$\text{Average} = 55.1 \text{ ug}$$

Using the average values measured for the number of grams of FC95 and FC143 The number of moles of FC95 and FC143 :

FC95

$$\frac{0.8 \cdot 10^{-6} \text{ g}}{538 \text{ g/mol}} = 1.5 \cdot 10^{-9} \text{ mol}$$

Eq. 3

FC143

$$\frac{55.1 \cdot 10^{-6} \text{ g}}{431 \text{ g/mol}} = 1.3 \cdot 10^{-7} \text{ mol}$$

Eq. 4

Assuming the air behaves as a mixture of ideal gases and the air is at standard pressure, the number of moles of air molecules in 280 liters of air at 20 °C is:

$$\frac{280 \text{ liters} \cdot 273 \text{ K}}{(22.414 \text{ liters/mol}) \cdot 363 \text{ K}} = 9.39 \text{ mol}$$

Eq. 5

The following equation then gives the minimum vapor pressure the fluorochemical salts must have to be measured by this experiment :

FC95

$$\frac{1.5 \cdot 10^{-9} \text{ mol}}{9.39 \text{ mol}} \cdot 760 \text{ torr} = 1.2 \cdot 10^{-7} \text{ torr}$$

Eq. 6

FC143

$$\frac{1.3 \cdot 10^{-7} \text{ mol}}{9.39 \text{ mol}} \cdot 760 \text{ torr} = 1.1 \cdot 10^{-5} \text{ torr}$$

Eq. 7

December 7, 1993

Dr. Jim Wolter
3M Environmental

Dear Dr. Wolter:

With respect to our telephone conversation on 12-6-93 concerning your document "Impinger Studies of Volatility of FC95 and FC143" faxed to me on 12-3-93, I am sending the following comments.

Part I: Volatilization of fluorochemicals from some aqueous solutions

With the vapor pressures which FC95 and FC143 are likely to have, it is difficult to believe that these salts would be removed by air passing through aqueous solutions except by two mechanisms. The first is entrainment where micro-droplets of water could carry material out of solution. A second mechanism would be appropriate in cases where the fluorochemical is dissolved in an aqueous solution containing surfactant. At surfactant concentrations near or even below the CMC (critical micelle concentration) the passage of air through the solution should lead to an appreciable production of foam bubbles. A number of processes involve foam fractionation to remove dissolved materials from solution and I believe that it is certainly possible in the present case with surfactant solutions (e.g., 500 ppm of CTAB, cetyltrimethylammonium bromide) to extract FC95 and/or FC143 under the conditions of these experiments.

Part II: Gas saturation attempt to measure vapor pressures of solid FC95 and FC143

Based on a minimum detection level, the vapor pressure calculations seem appropriate (except for a trivial question about molecular weights: FC143 seems to have an ammonium counterion and FC95 seems to have a potassium counterion?). The calculated vapor pressures are semi-plausible but I don't think that the experimental conditions provide firm evidence that the numbers are reasonable. A crucial point in the gas saturation method is the attainment of vapor equilibrium with the flowing gas. With no detectable signal, one does not have a handle on this question. In the general sense, it would be highly desirable to have a reference substance with known vapor pressure done in a similar experiment. From the brief literature reading which I have done, it appears that the gas saturation method is not recommended for determination of vapor pressures below a few millitorr. Knudsen effusion might be employed in the case of very low vapor pressures. Since these fluorochemicals are very stable, a possible alternative procedure would be to repeat the gas saturation experiment at substantially higher temperatures such as 100 to 150 deg. C, for example. Finding measurable signals in such a range should enable extrapolation to a room temperature vapor pressure.

Sincerely yours,



Edwin E. Tucker, Ph. D.
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Norman, OK 73019
Tel. (405) 325-2054; Fax (405) 325-6111

06/16/2000

ENVIRONMENTAL LABORATORY
ARCHIVED FINAL REPORT

LAB REQUEST NO. L3306
REQUESTOR NAME: JDJ
DEPARTMENT: 0222
PROJECT NO: 06
DATE RECEIVED: 12/13/1993
DESC: VOLATILITY OF FC95 AND FC143

CONTRACT LAB(S):
EXP COMP DATE: 12/17/1993
DATE COMPLETED: 12/15/1993
PROJECT LEAD:
PHONE NO:
3M FAX NO: 651-778-6176

Impinger study I.

SAMPLE	DATE	CODE	DESCRIPTION	RESULT	MDL or (95% C.I.)
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JTW-SPEC	SPECIAL STUDY - JTW	COMPLETE
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