

SUPPLEMENTARY MATERIALS

Development and Validation of a LC-MS/MS Method for Determination of Multi-class Antibiotic Residues in Aquaculture and River Waters, and Photocatalytic Degradation of Antibiotics by TiO₂ Nanomaterials.

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Figure S1-S10: Optimization of MS-MS parameters for antibiotic analysis.

S1. The result autotune of optimum MS-MS parameters of amoxicillin (AMOX), ampicillin (AMPI), lincomycin (LCM), trimethoprim (TMTP).

Results

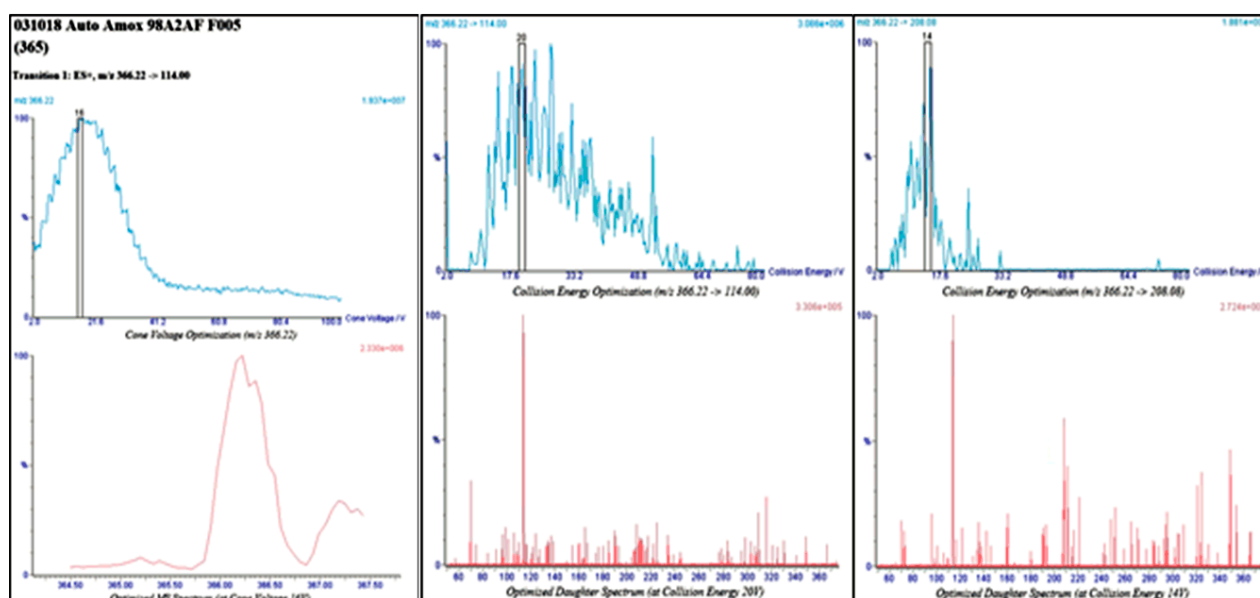
IntelliStart generated the following experiments:

MRM Experiment E:\MASSLYNX PROJECT\QUOC DUY.PRO\AUTOTUNE\Van-Co-Ate\031018 Auto Function 2 Amox-Ampi-Linco-Trime 98A2AF F005 L2.exp

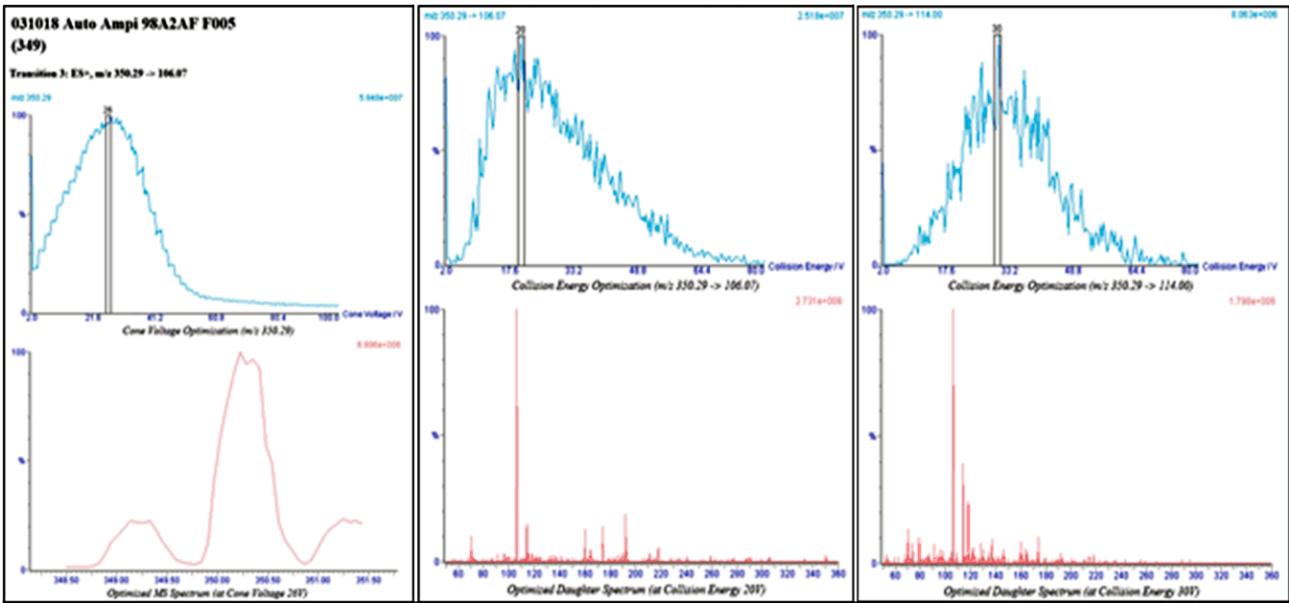
IntelliStart found the following compounds:

Compound	Formula/Mass		Parent m/z	Cone Voltage	Daughters	Collision Energy	Ion Mode
031018 Auto Amox 98A2AF F005	365	1	366.22	16	114.00	20	ES+
		2	366.22	16	208.08	14	ES+
031018 Auto Ampic 98A2AF F005	349	1	350.29	26	106.07	20	ES+
		2	350.29	26	114.00	30	ES+
031018 Auto Linco 407 98A2AF F005	406	1	407.35	42	126.16	28	ES+
		2	407.35	42	359.20	18	ES+
031018 Auto Trime 98A2AF F005	290	1	291.29	48	230.13	22	ES+
		2	291.29	48	123.05	24	ES+

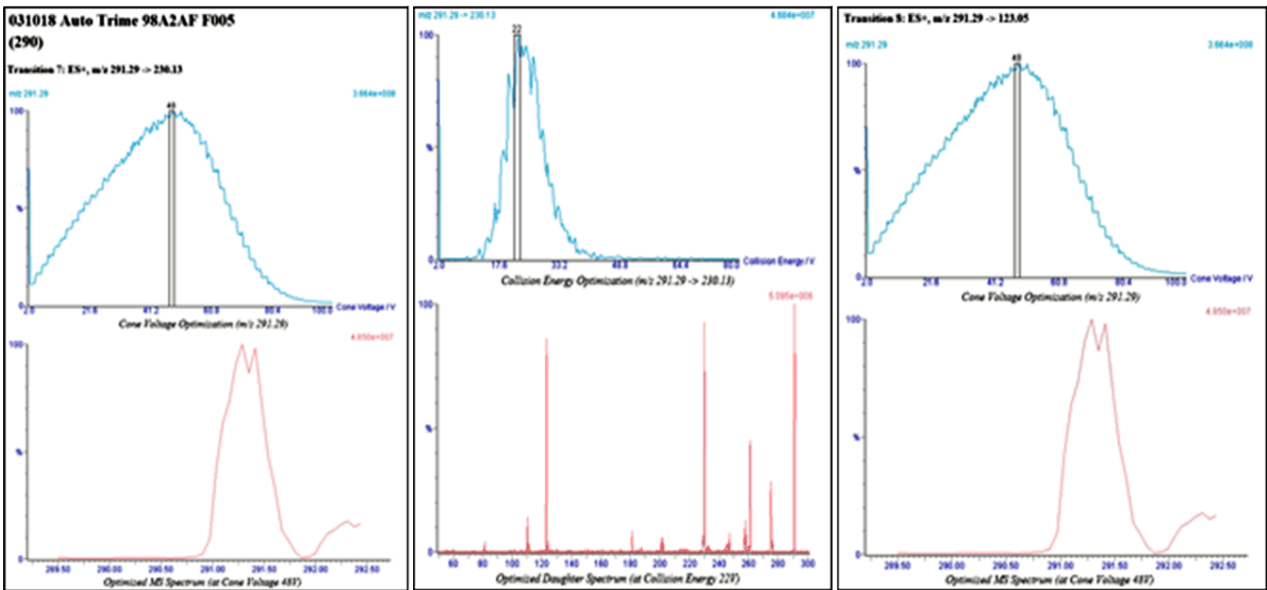
S2. Optimum MS-MS parameters of ampicilline (AMPI).



S3. Optimum MS-MS parameters of ampicilline (AMPI).



S4. Optimum MS-MS parameters of trimethoprim (TMTP).



S5. The result autotune of optimum MS-MS parameters of sulfamethazine (SMZ), sulfamethoxazole (SMZX).

Results

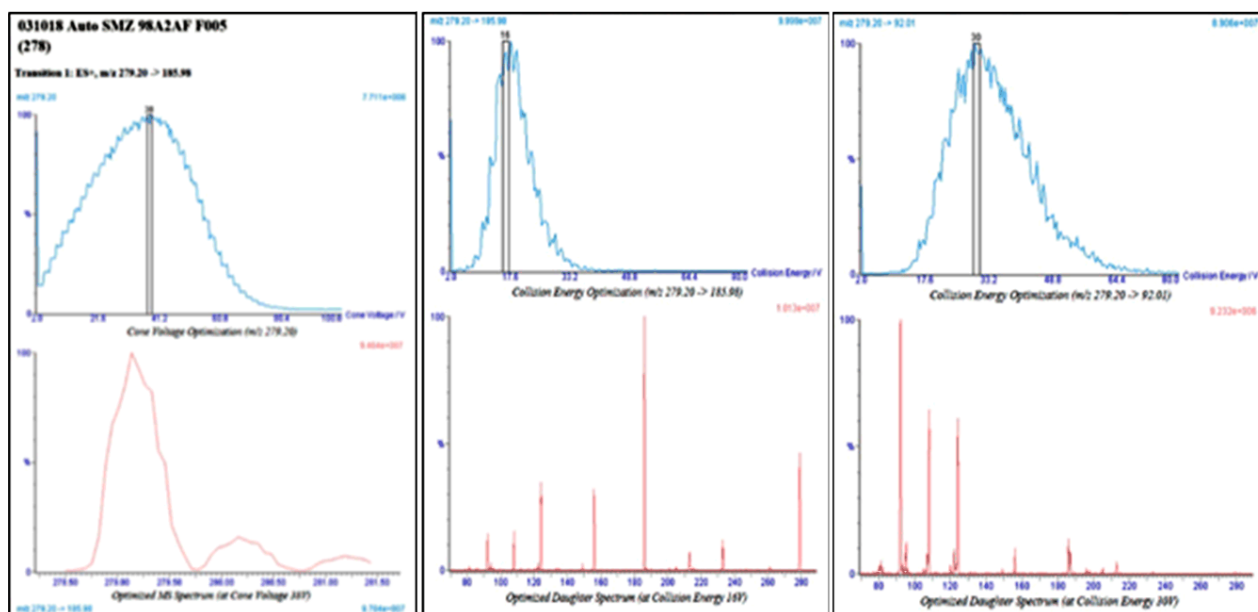
IntelliStart generated the following experiments:

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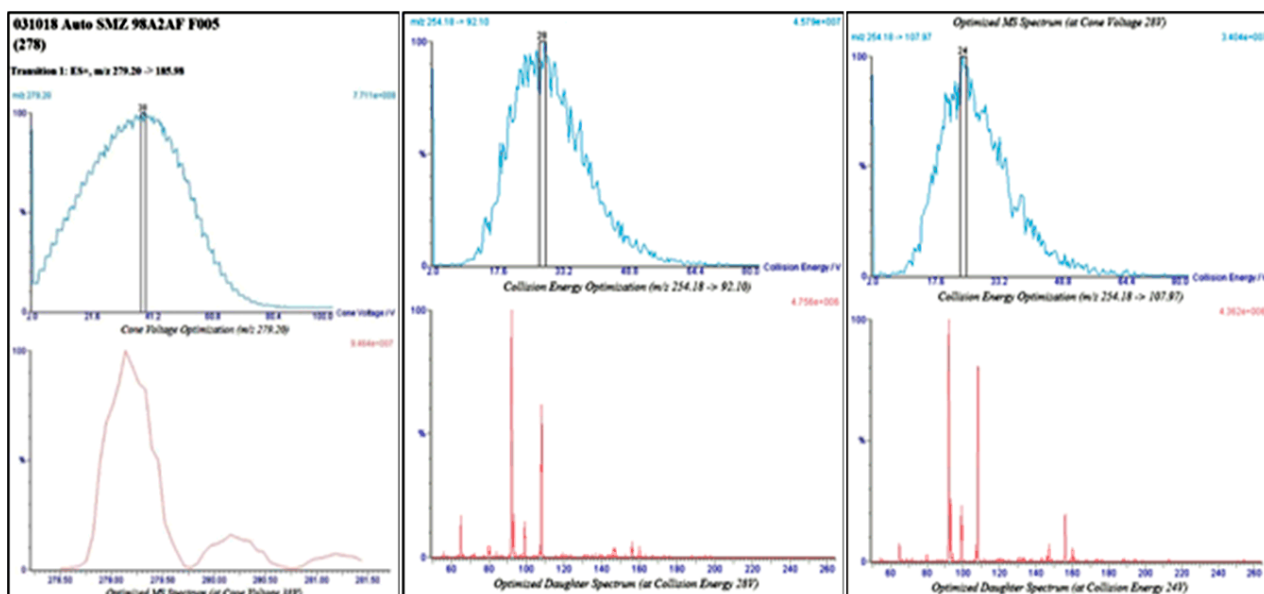
IntelliStart found the following compounds:

Compound	Formula/Mass		Parent m/z	Cone Voltage	Daughters	Collision Energy	Ion Mode
031018 Auto SMZ 98A2AF F005	278	1	279.22	36	186.06	16	ES+
		2	279.22	36	92.04	30	ES+
031018 Auto SMZX 98A2AF F005	253.4	1	254.18	30	92.10	28	ES+
		2	254.18	30	107.97	22	ES+

S6. Optimum MS-MS parameters of sulfamethazine (SMZ).



S7. Optimum MS-MS parameters of Sulfamethoxazole (SMZX).



S8. The result autotune of optimum MS-MS parameters of vancomycin (VCM), atenolol-IS (ATN).

Results

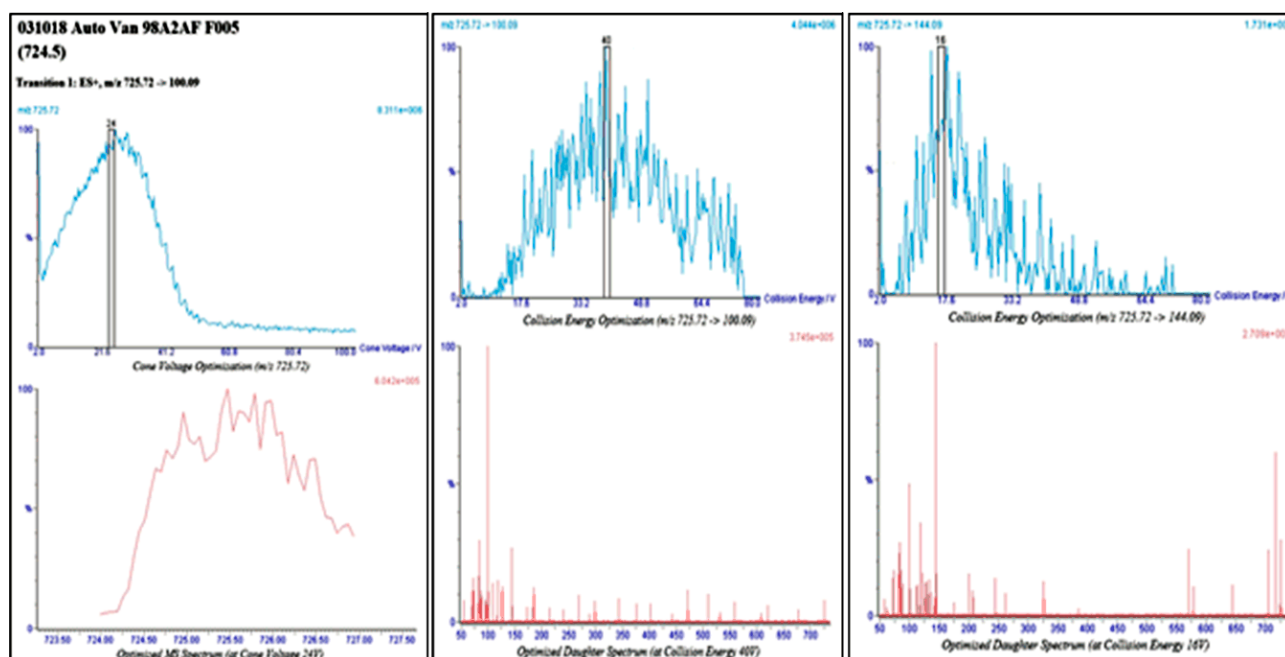
IntelliStart generated the following experiments:

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IntelliStart found the following compounds:

Compound	Formula/Mass		Parent m/z	Cone Voltage	Daughters	Collision Energy	Ion Mode
031018 Auto Van 98A2AF F005	724.5	1	725.72	24	100.09	40	ES+
		2	725.72	24	144.09	16	ES+
031018 Auto Ate 98A2AF F005	266	1	267.29	38	71.62	22	ES+
		2	267.29	38	56.01	32	ES+

S9. Optimum MS-MS parameters of Vancomycin (VCM).



S10. Optimum MS-MS parameters of Atenolol (ATN).

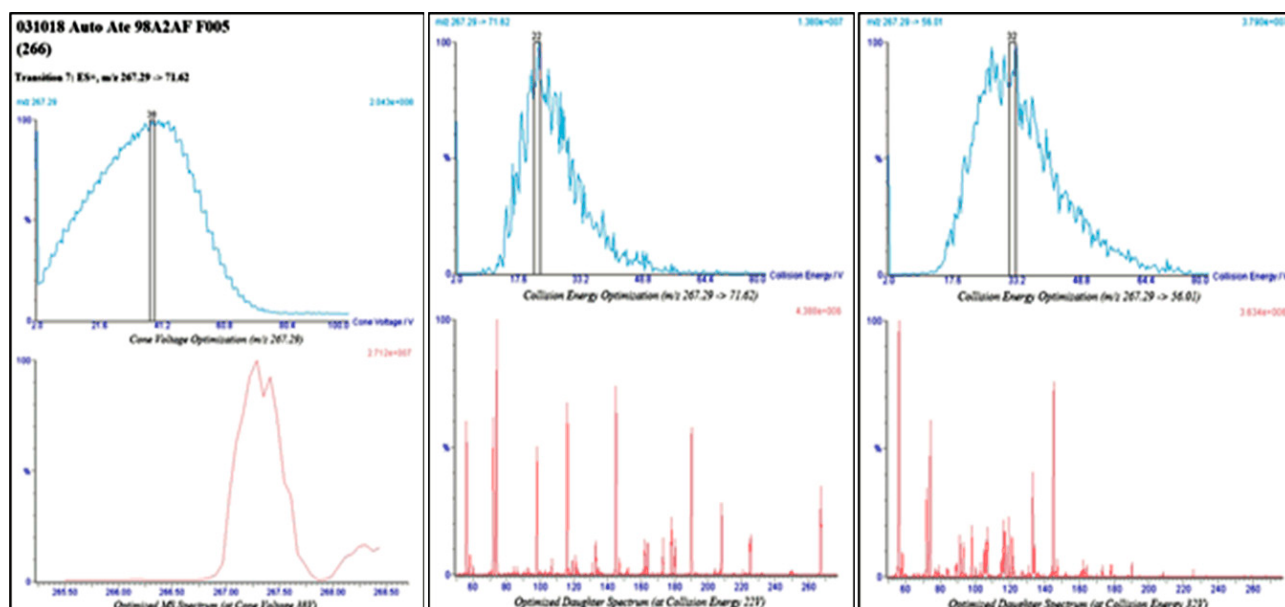
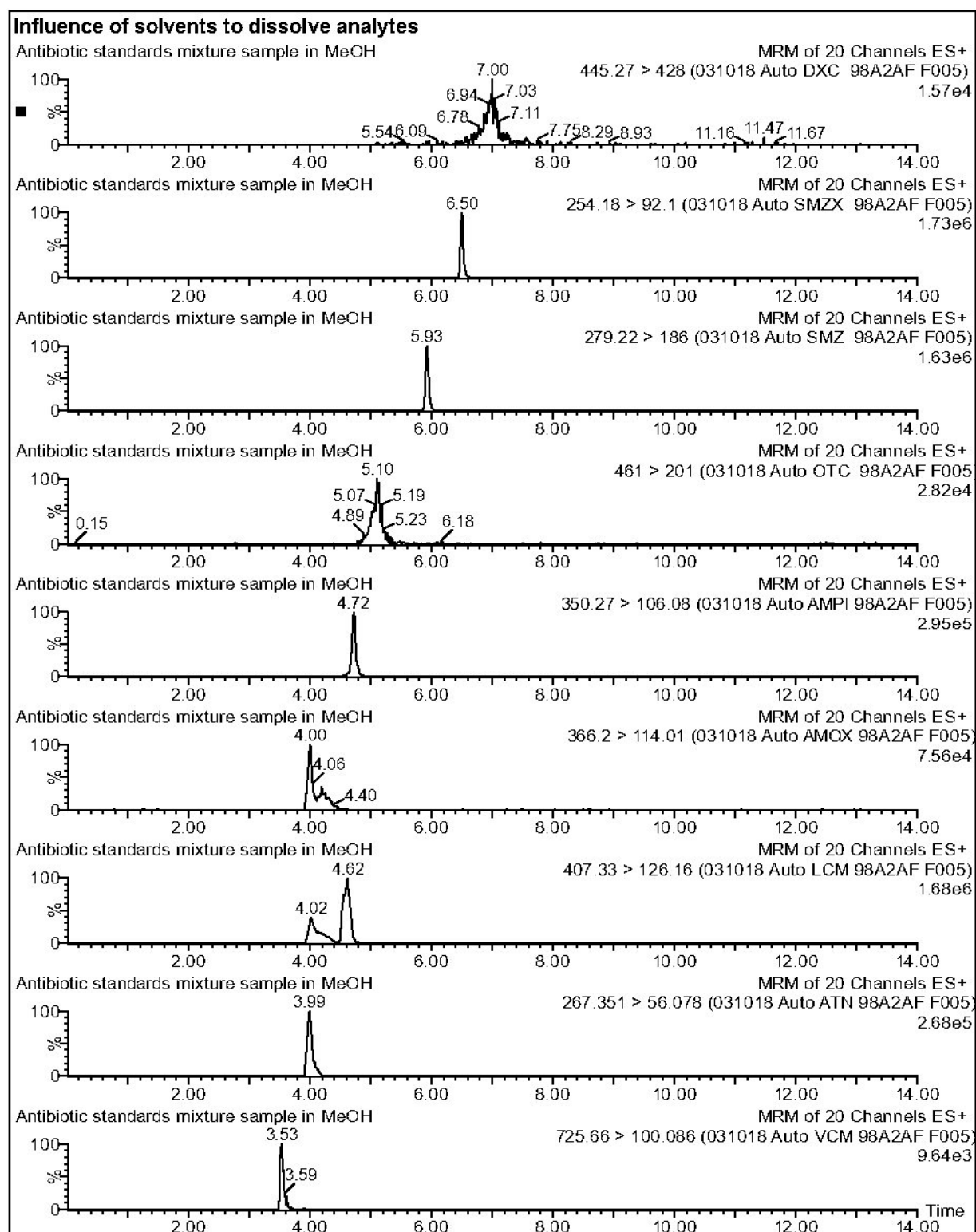
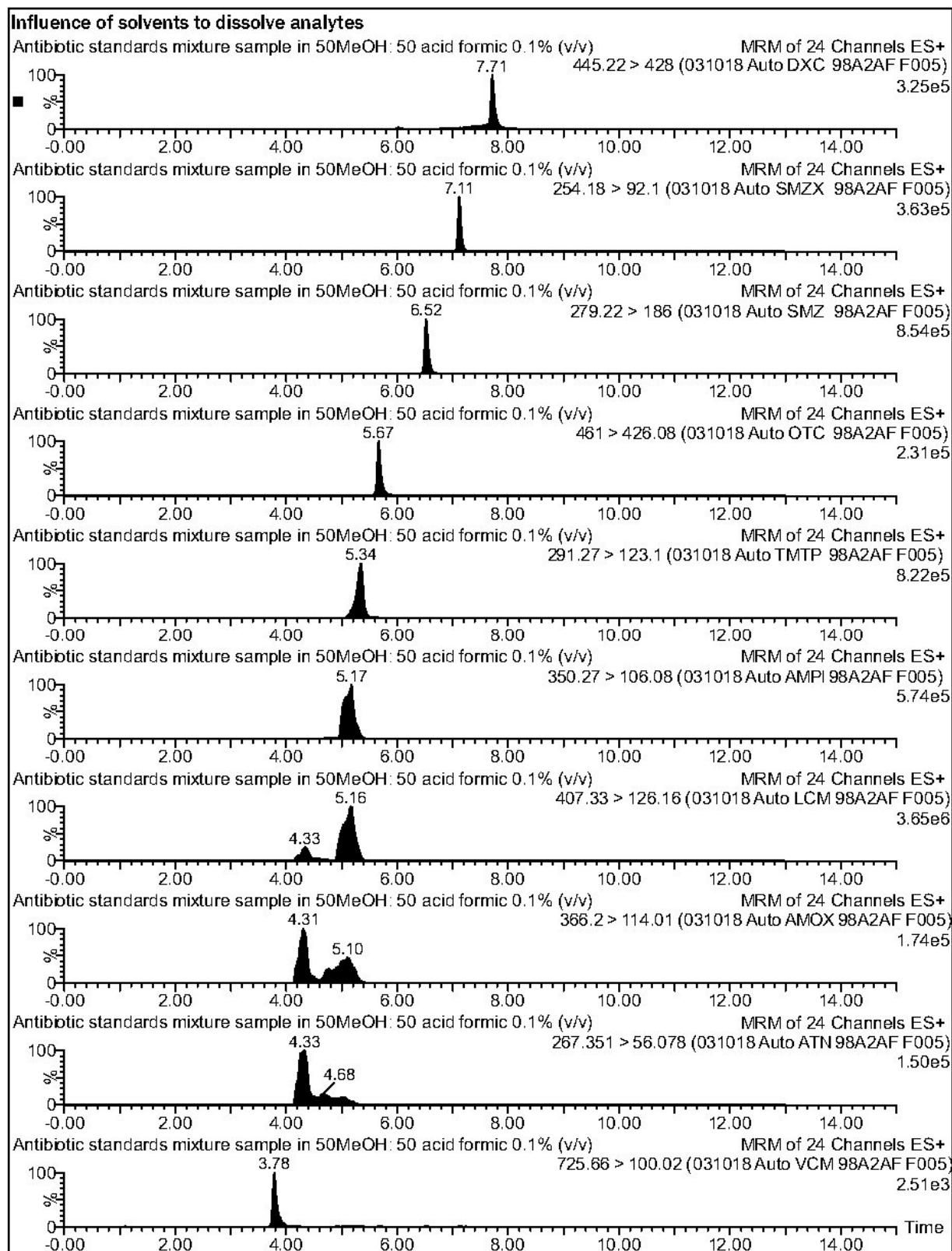


Figure S11-S14: Chromatograms indicated the effects of solvents on dissolve analytes.

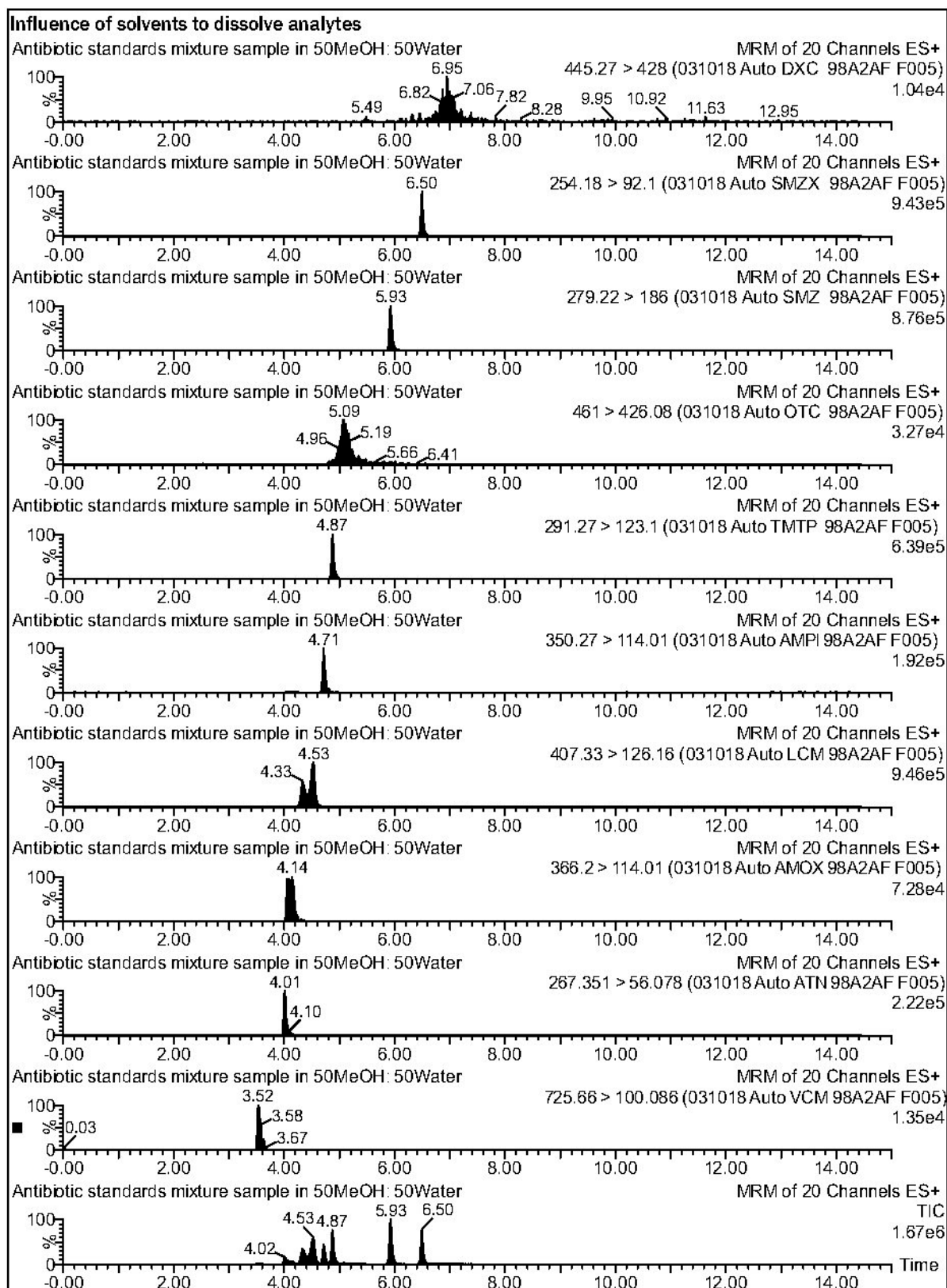
S11. Standard antibiotic mixture in MeOH.



S12. Standard antibiotic mixture in 50 MeOH: 50 formic acid 0.1% in water (v/v).



S13. Standard antibiotic mixture in 50 MeOH: 50 water.



S14. Standards antibiotic mixture in water- formic acid (999:1).

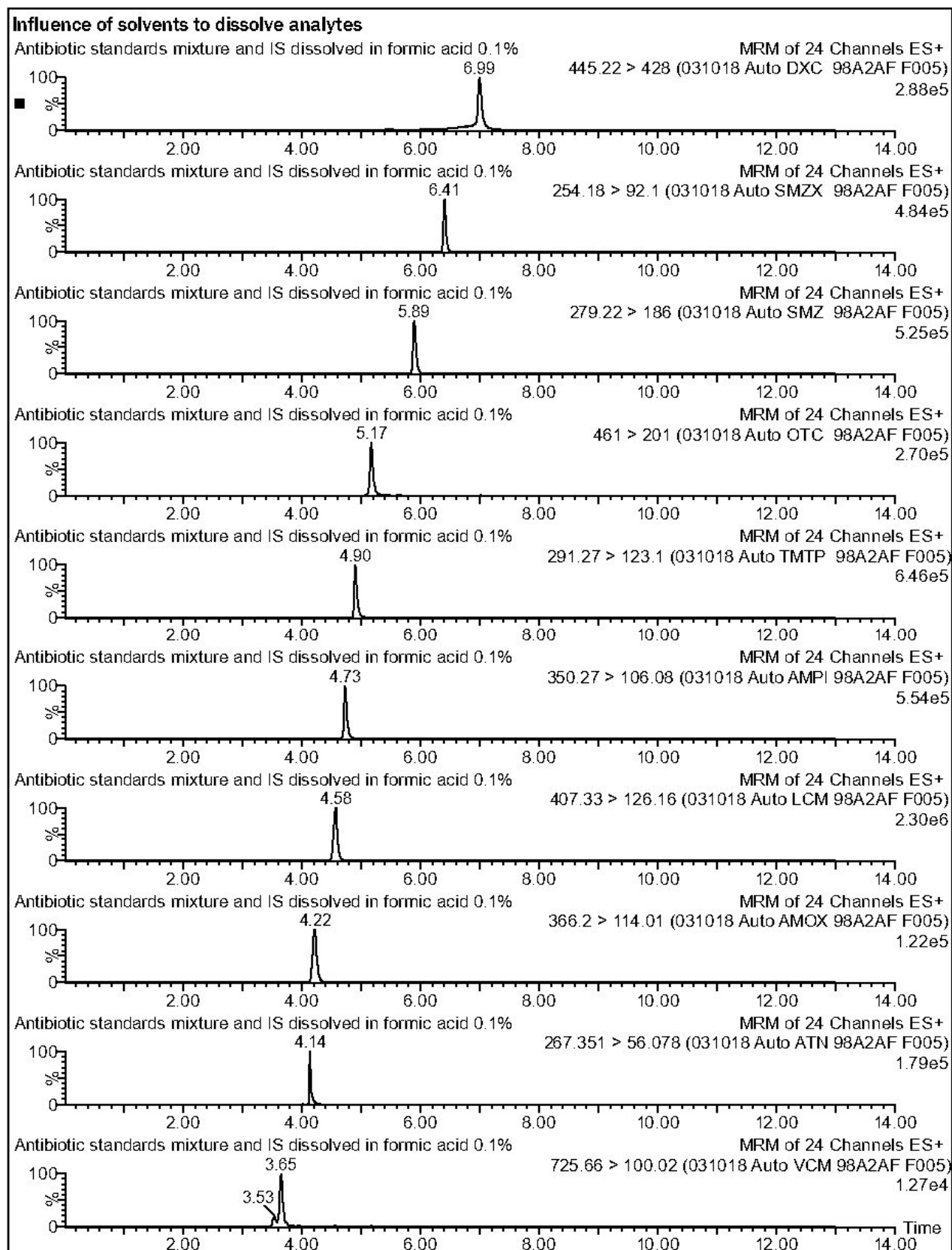
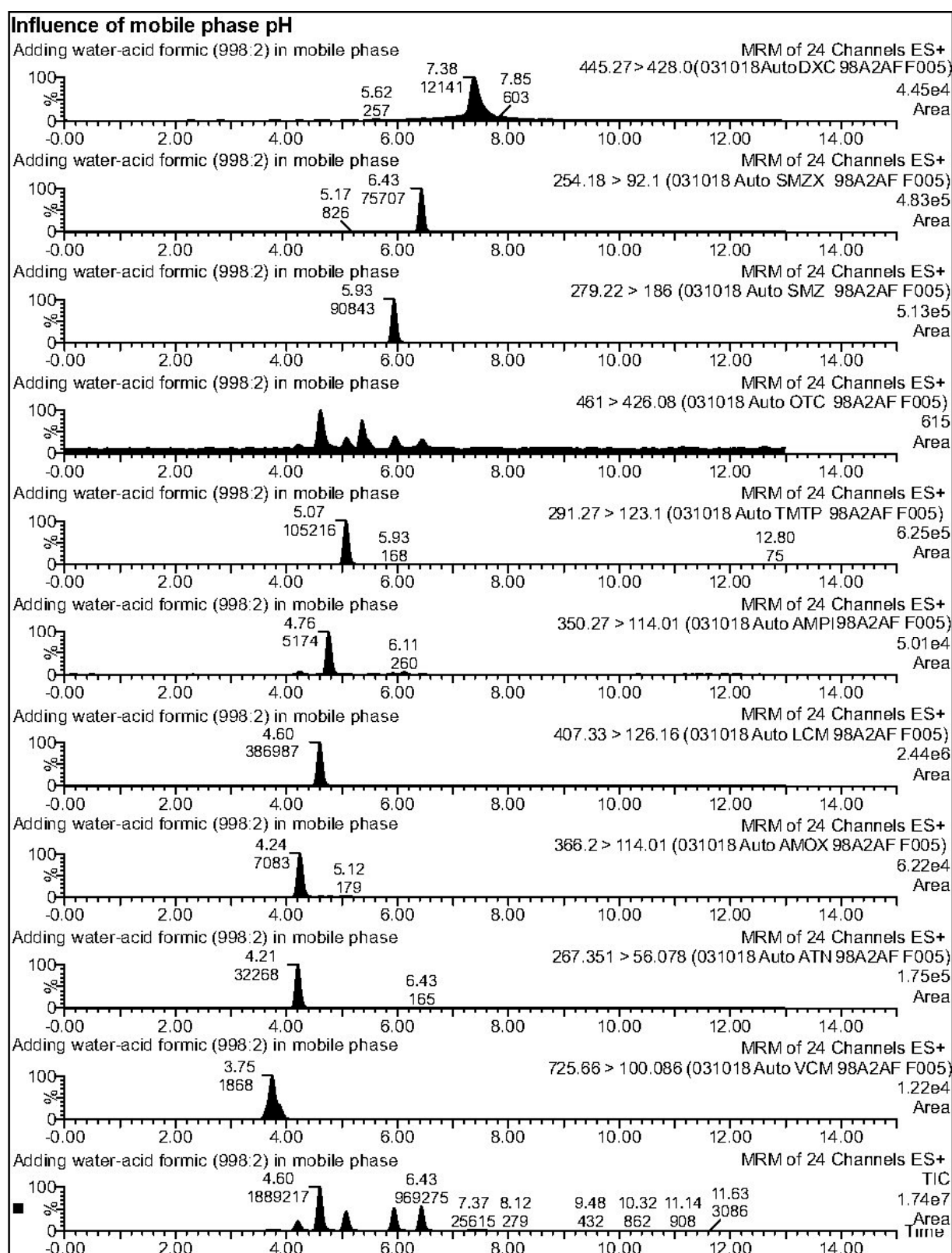
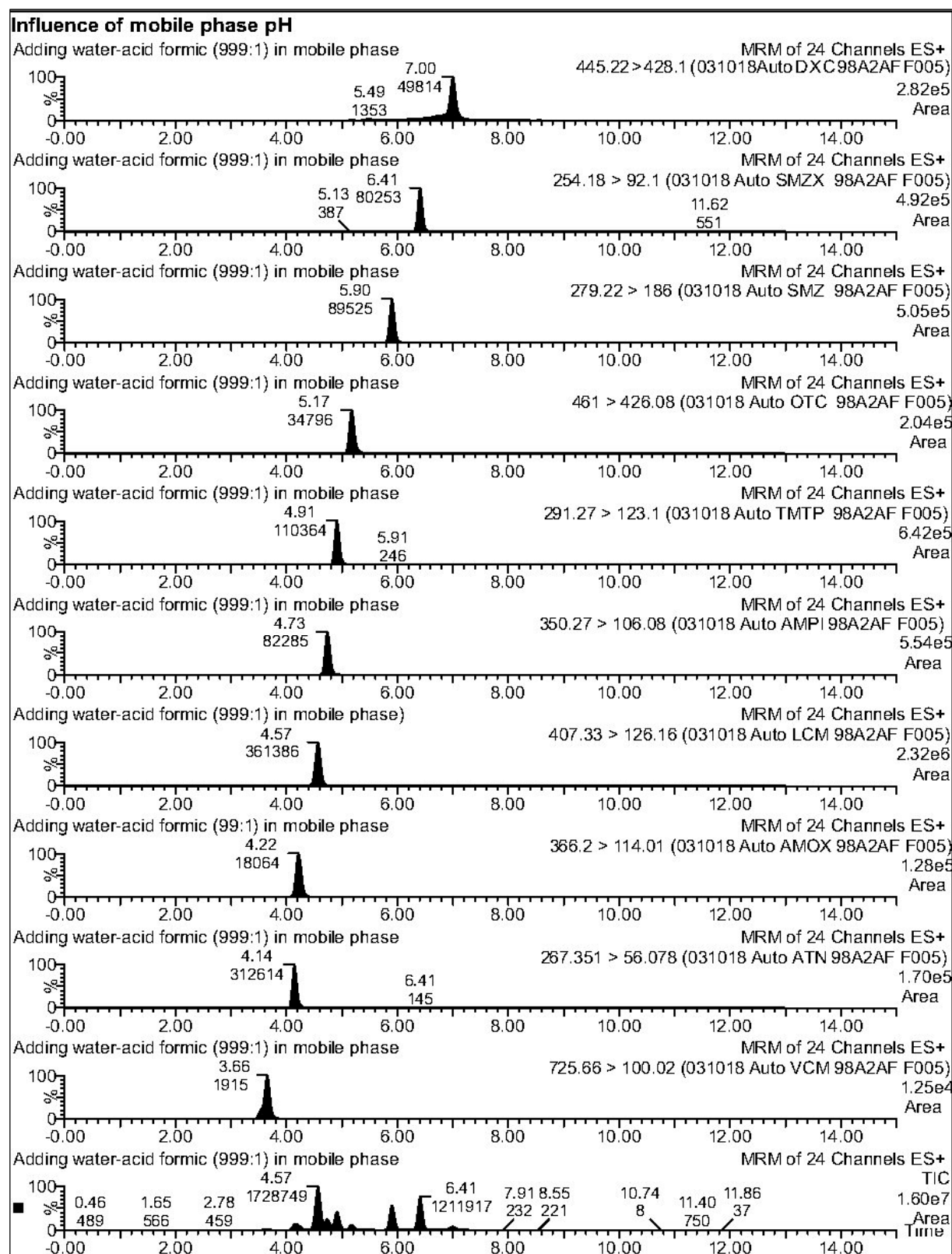


Figure S15-S16: Chromatograms indicated influence of mobile phase pH.

S15. Adding water-acid formic (998:2) in mobile phase.

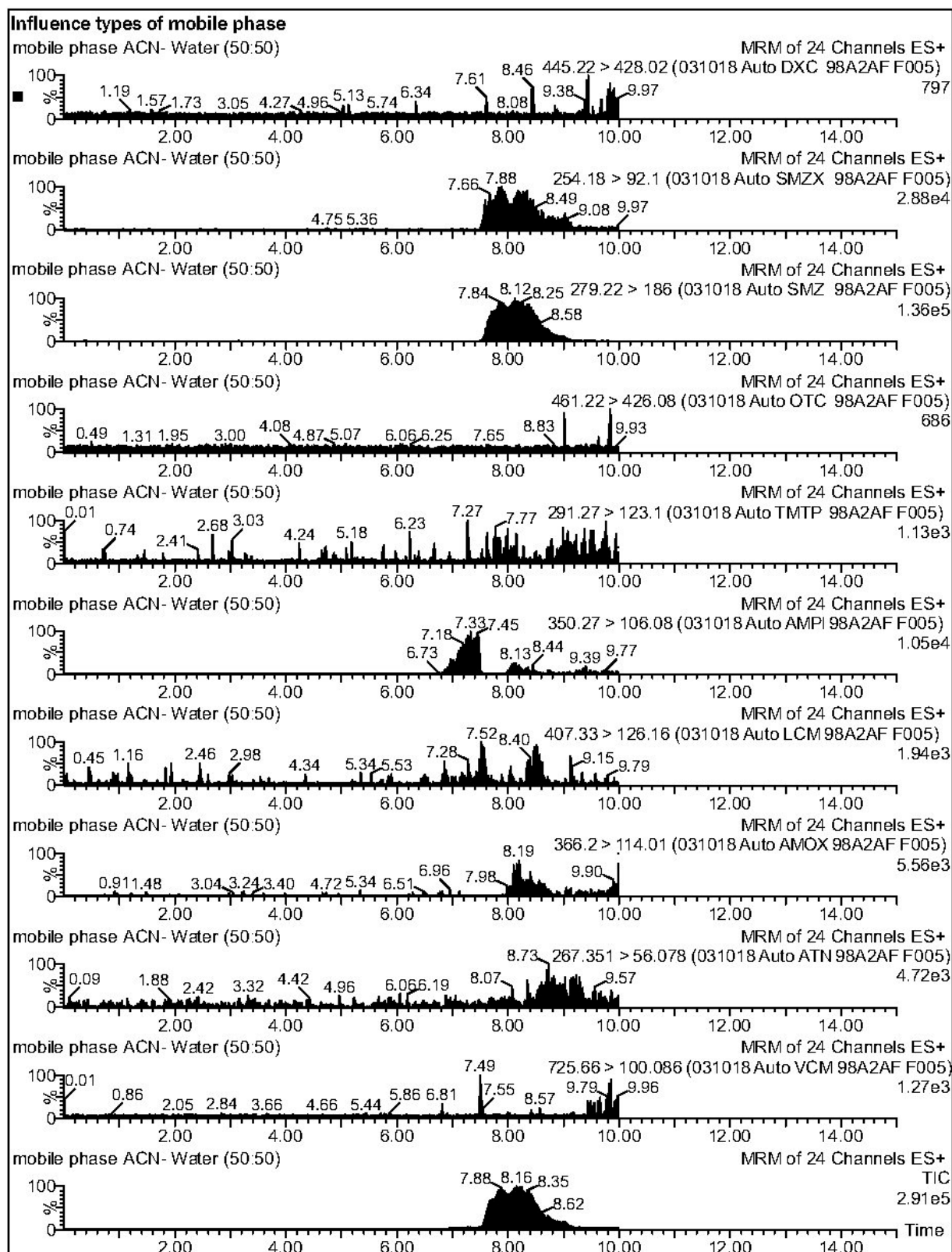


S16. Adding water-acid formic (999:1) in mobile phase.

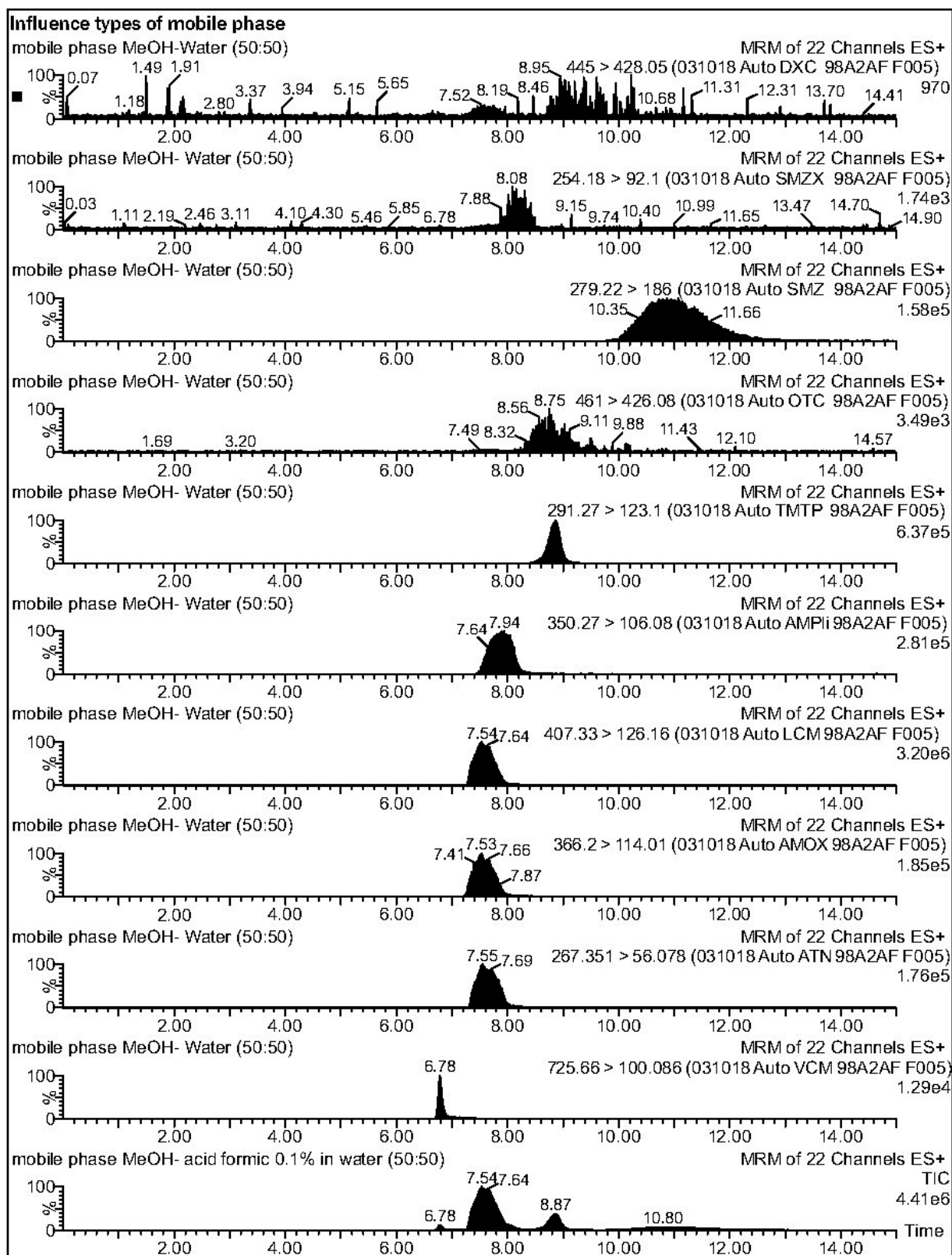


Figures S17-S19: Chromatograms indicated influence of mobile phase types

S17. Mobile phase of ACN- water (50:50).



S18. Mobile phase of MeOH-water (50:50).



S19. Mobile phase of MeOH-acid formic 0.1% (50:50).

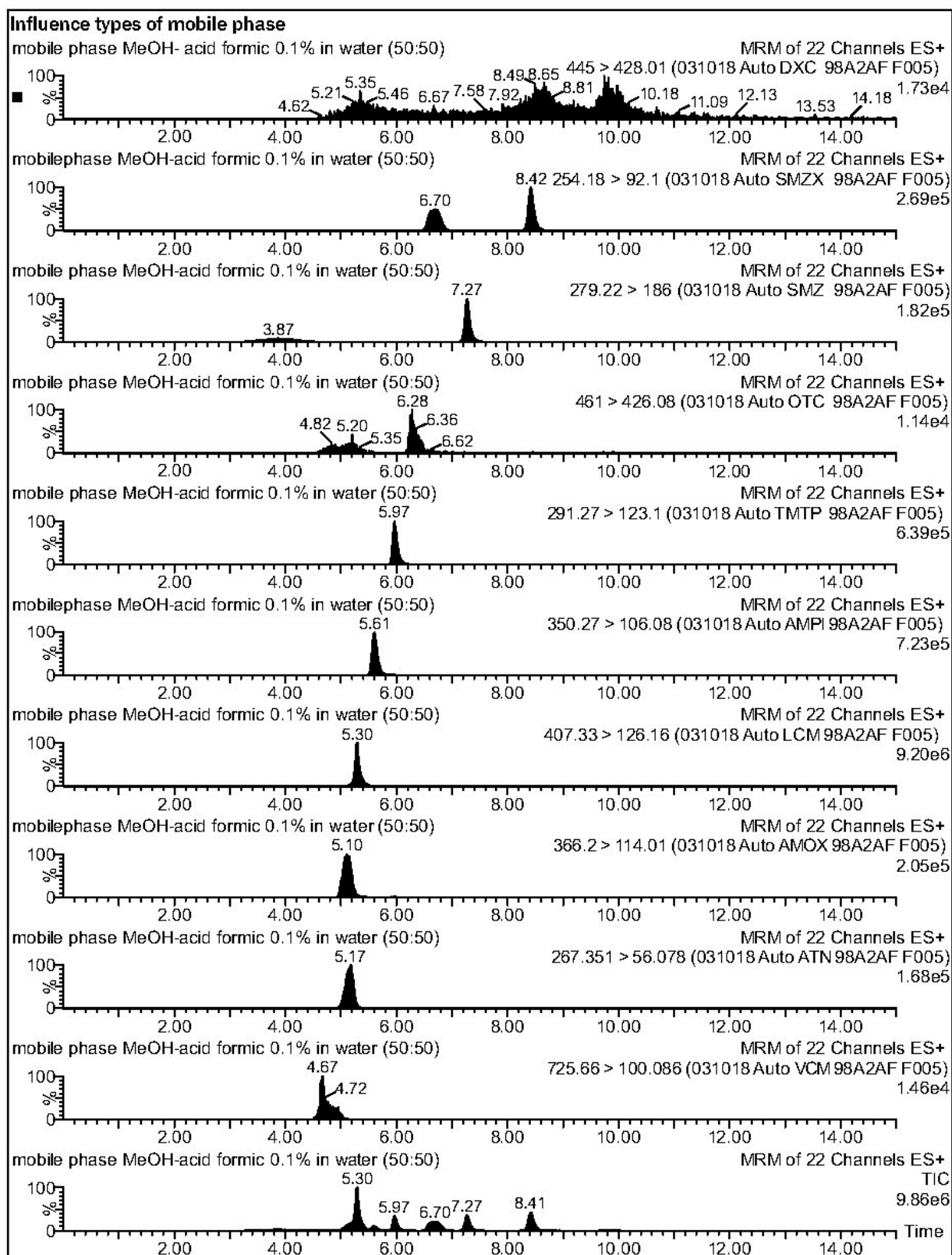
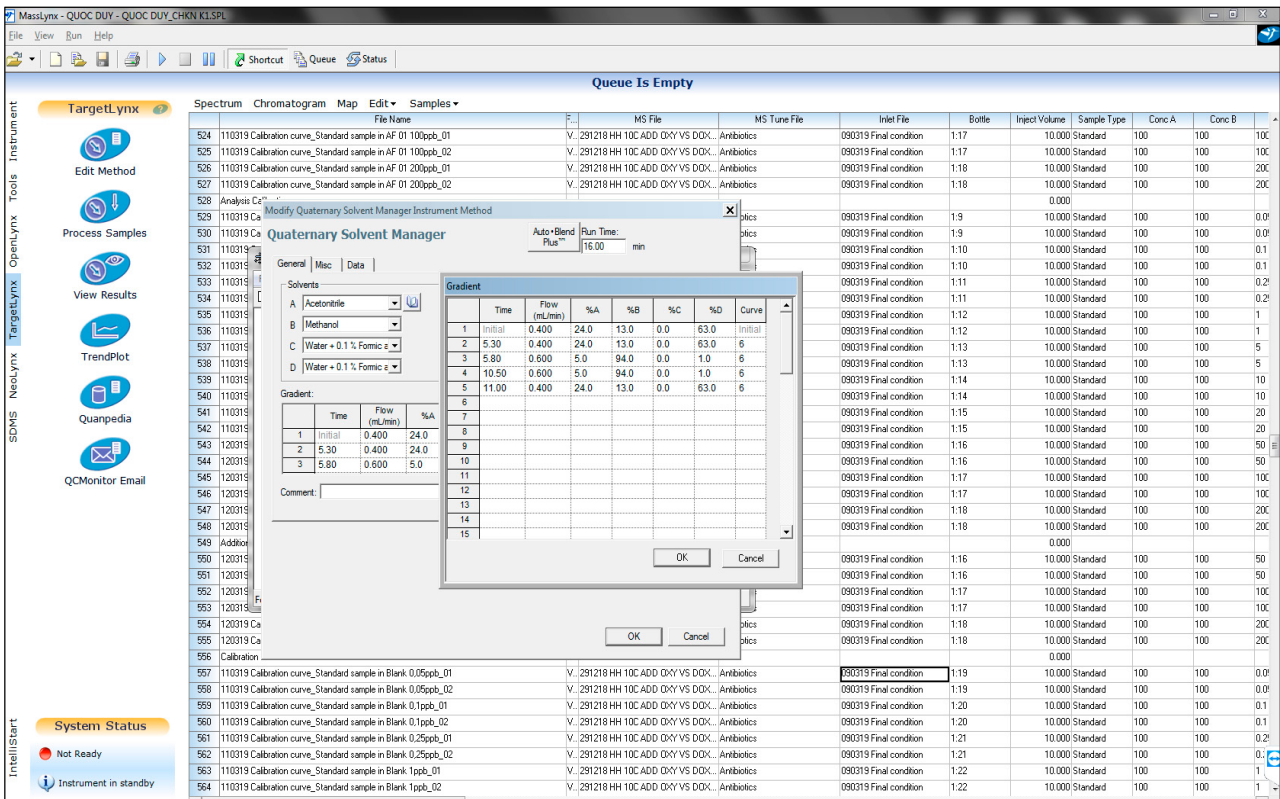
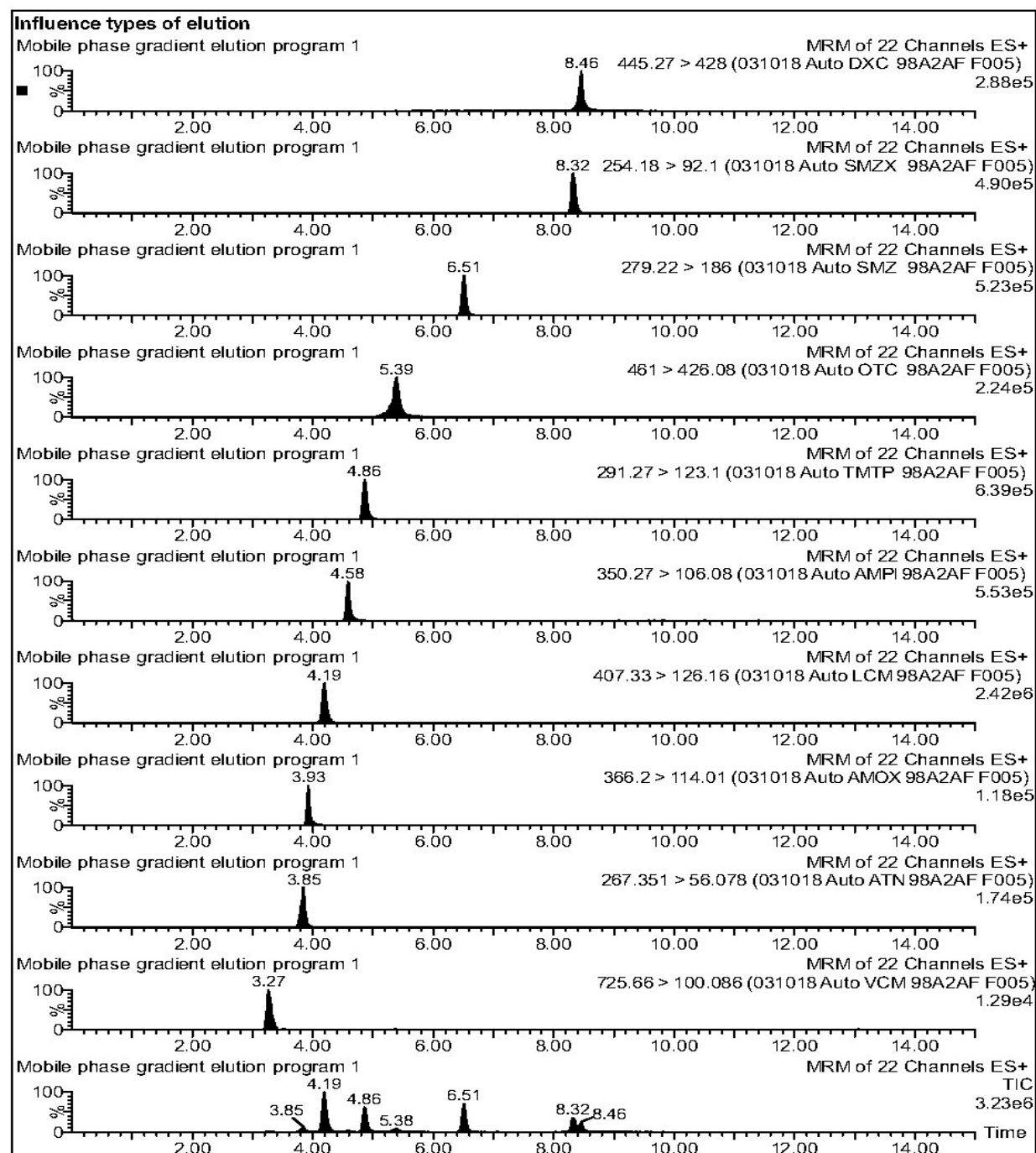


Figure S20-S21: Chromatograms indicated influence of elution program
S20A. Gradient program 1 of mobile phase.



S20B. LC-MS/MS chromatogram at gradient program 1 of mobile phase.



S21A. Gradient program 2 of mobile phase.

TargetLynx

SDMS NeoLynx TargetLynx OpenLynx Tools Instrument

Edit Method

Process Samples

View Results

TrendPlot

Quandpedia

QCMonitor Email

Spectrum Chromatogram Map Edit Samples

File Name

MS File

MS Tune File

Inlet File

Bottle

Inject Volume

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7	041018 HHC G2	K:\E:\MASS\...HHC Auto 98A2AF F005 G2 15m	Default	041018 Gradient 2	1:1	10.000
8	041018 HHC G3	K:\E:\MASS\...HHC Auto 98A2AF F005 G3 15m	Default	041018 Gradient 2	1:1	10.000
9	041018 HHC G4	K:\E:\MASS\...HHC Auto 98A2AF F005 G4 15m	Default	041018 Gradient 2	1:1	10.000
10	041018 HHC G5	K:\E:\MASS\...HHC Auto 98A2AF F005 G5 15m	Default	041018 Gradient 2	1:1	10.000
11	041018 HHC G6	K:\E:\MASS\...HHC Auto 98A2AF F005 G6 15m	Default	041018 Gradient 2	1:1	10.000
12	041018 HHC G7	K:\E:\MASS\...HHC Auto 98A2AF F005 G7 15m	Default	041018 Gradient 2	1:1	10.000
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22	041018 HHC G17	K:\E:\MASS\...HHC Auto 98A2AF F005 G17 15m	Default	041018 Gradient 2	1:1	10.000
23	041018 HHC G18	K:\E:\MASS\...HHC Auto 98A2AF F005 G18 15m	Default	041018 Gradient 2	1:1	10.000
24	041018 HHC G19	K:\E:\MASS\...HHC Auto 98A2AF F005 G19 15m	Default	041018 Gradient 2	1:1	10.000
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35	081018 HHC G30	K:\E:\MASS\...HHC Auto 98A2AF F005 G30 15m	Default	081018 Gradient 2	1:1	10.000
36	081018 HHC G31	K:\E:\MASS\...HHC Auto 98A2AF F005 G31 15m	Default	081018 Gradient 2	1:1	10.000
37	081018 HHC G32	K:\E:\MASS\...HHC Auto 98A2AF F005 G32 15m	Default	081018 Gradient 2	1:1	10.000
38	091018 HHC G33	K:\E:\MASS\...HHC Auto 98A2AF F005 G33 15m	Default	091018 Gradient 2	1:1	10.000

Queue Is Empty

Modify Quaternary Solvent Manager Instrument Method

Quaternary Solvent Manager

Auto Blend Plus Run Time: 14.00 min

General Misc Data

Solvents

A Acetonitrile

B Methanol

C Water

D Water + 0.1 % Formic acid

Gradient

	Time	Flow (mL/min)	%A	%B	%C	%D	Curve
1	Initial	0.300	23.0	10.0	0.0	67.0	Initial
2	7.00	0.500	20.0	30.0	0.0	50.0	6
3	9.00	0.500	80.0	0.0	0.0	20.0	6
4	13.50	0.300	25.0	12.0	0.0	63.0	6
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							

Gradient

	Time	Flow (mL/min)	%A
1	Initial	0.300	23.0
2	7.00	0.500	20.0
3	9.00	0.500	80.0

Comment:

OK Cancel

S21B. LC-MS/MS chromatogram at gradient program 2 of mobile phase.

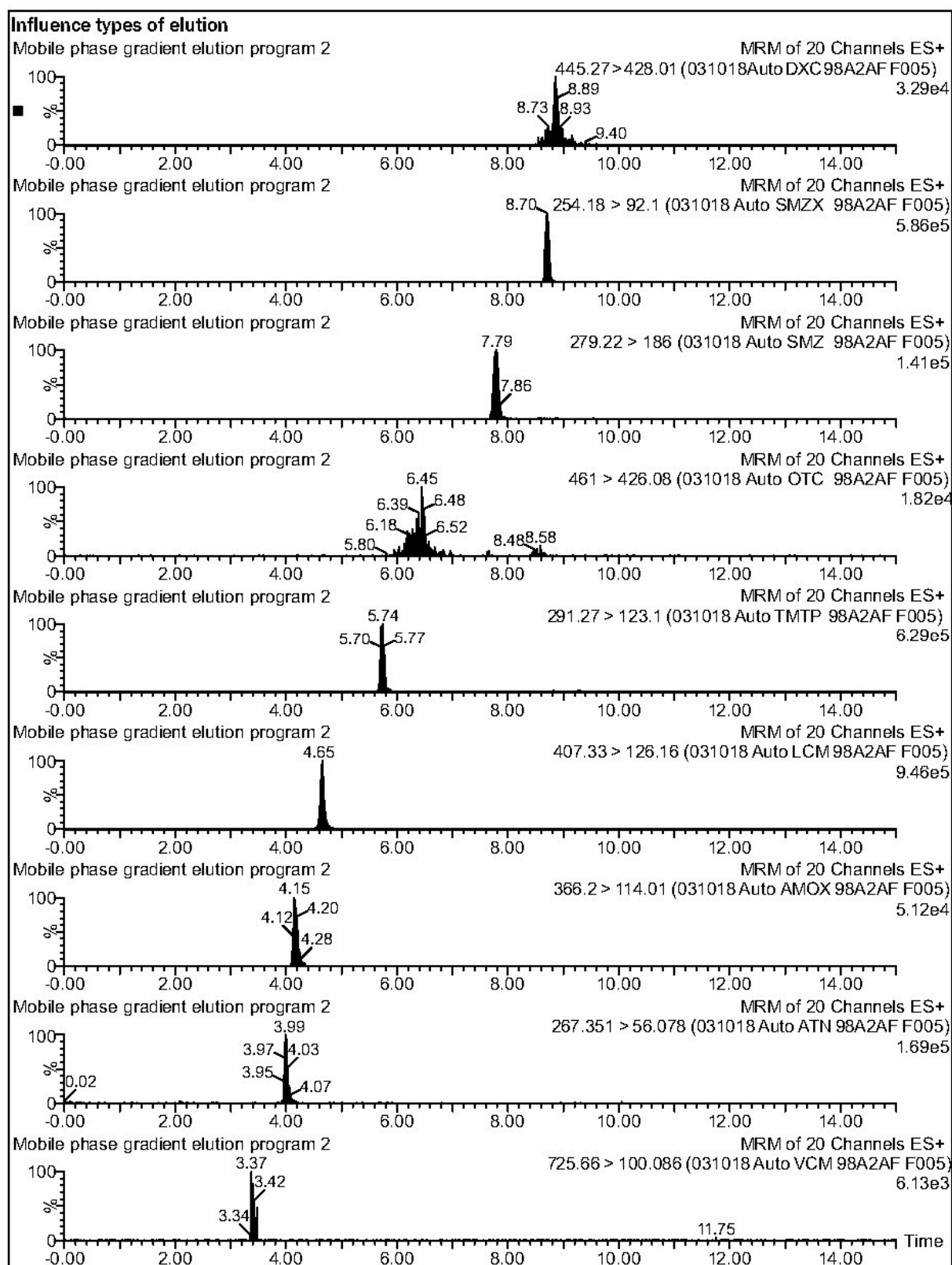
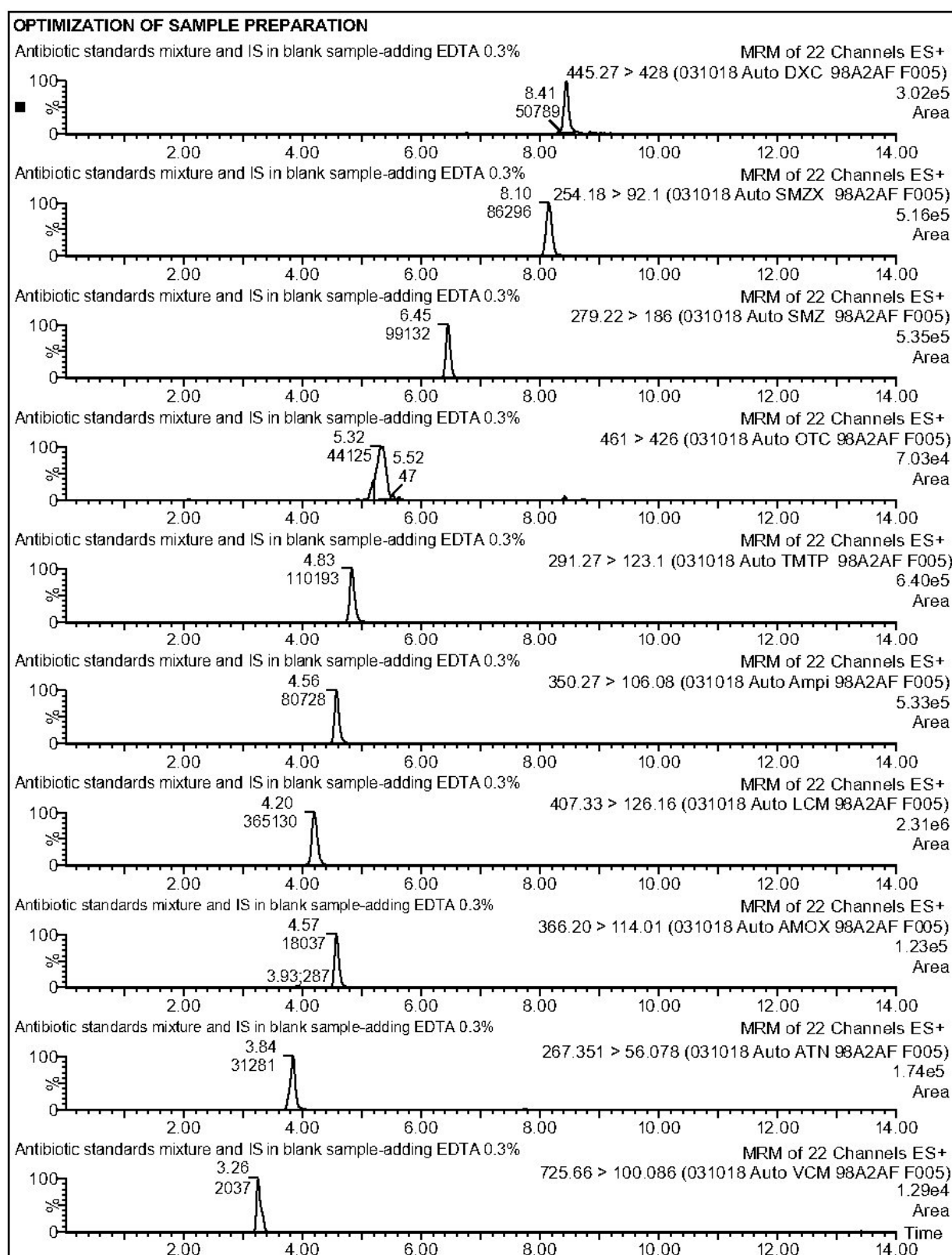
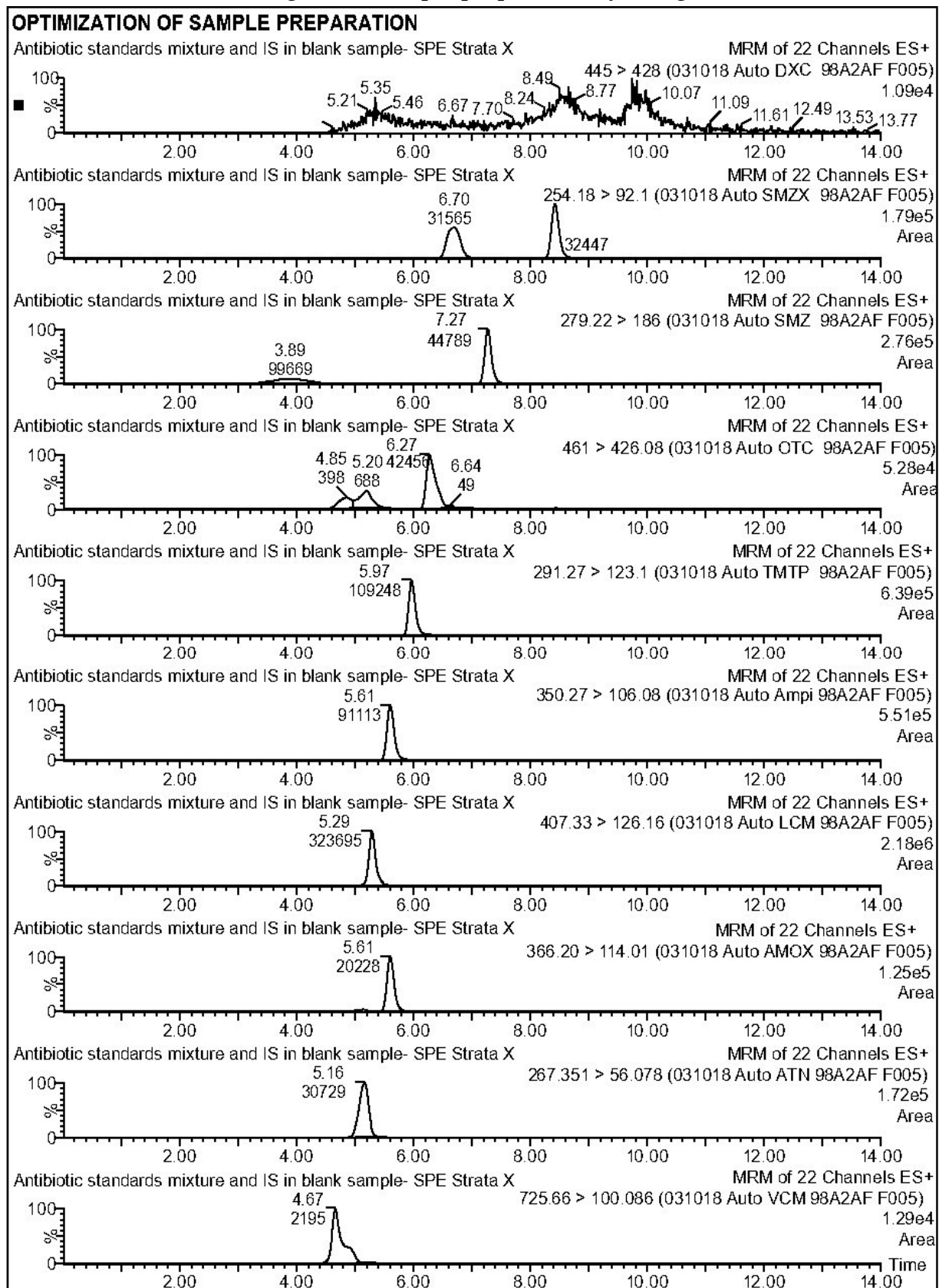


Figure S22-S25: Chromatograms present the investigation of sample preparation

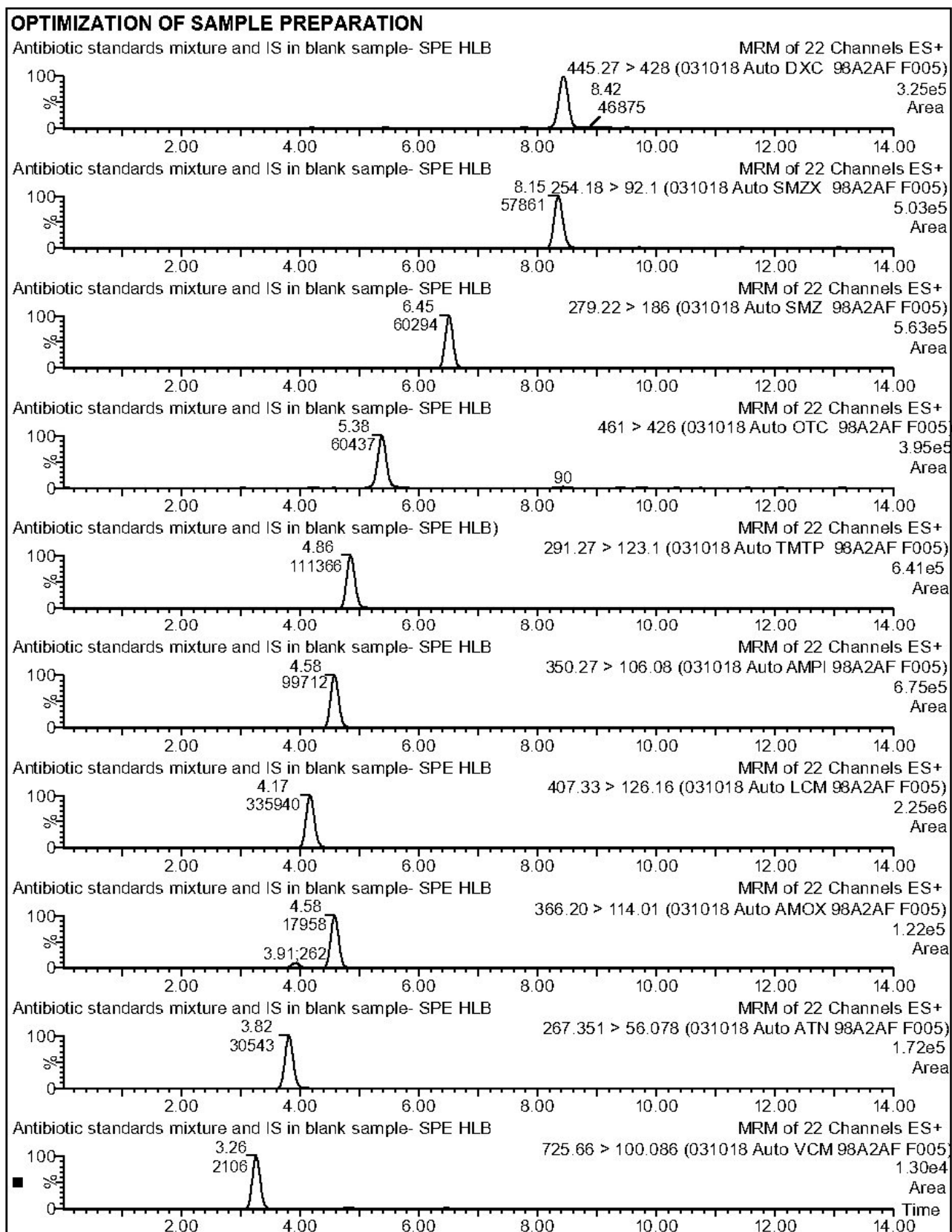
S22. LC-MS/MS chromatogram of sample preparation by adding EDTA 0.3%.



S23. LC-MS/MS chromatogram of sample preparation by using SPE-Strata X.



S24. LC-MS/MS chromatogram of sample preparation by using SPE-Oasis HLB.



S25. LC-MS/MS chromatogram of sample preparation by adding EDTA 0.3% + SPE-HLB.

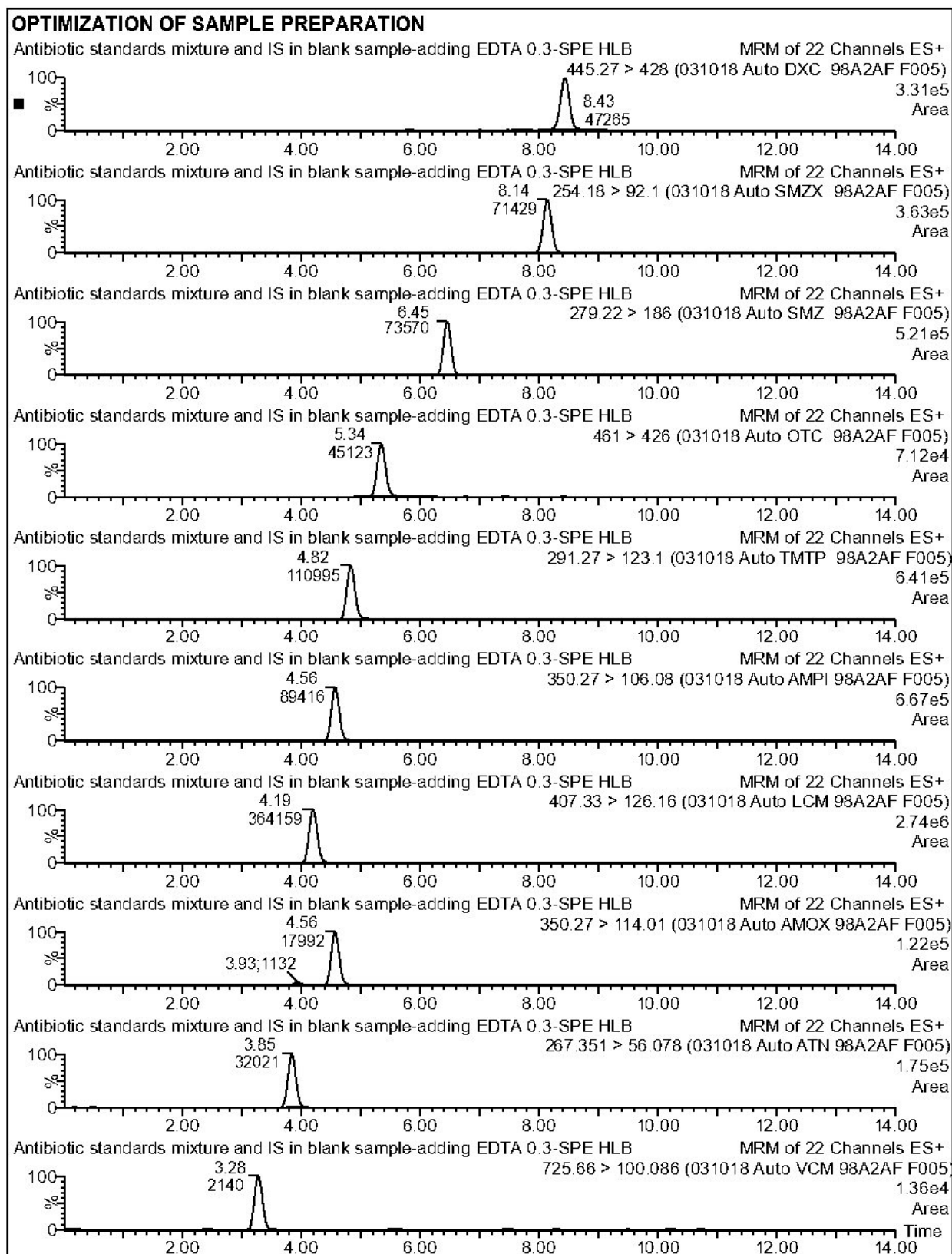
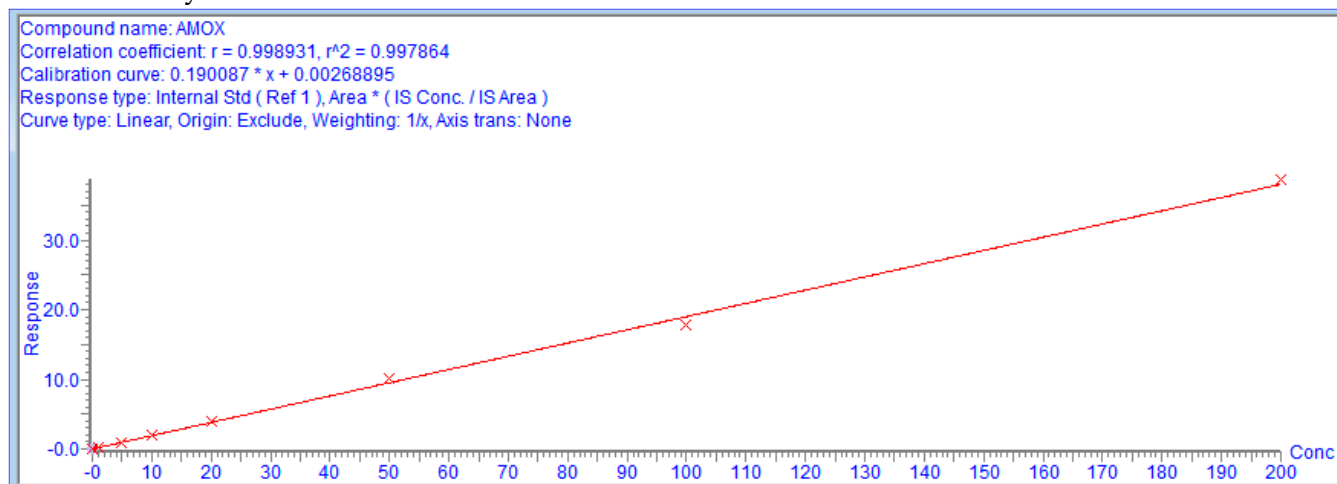
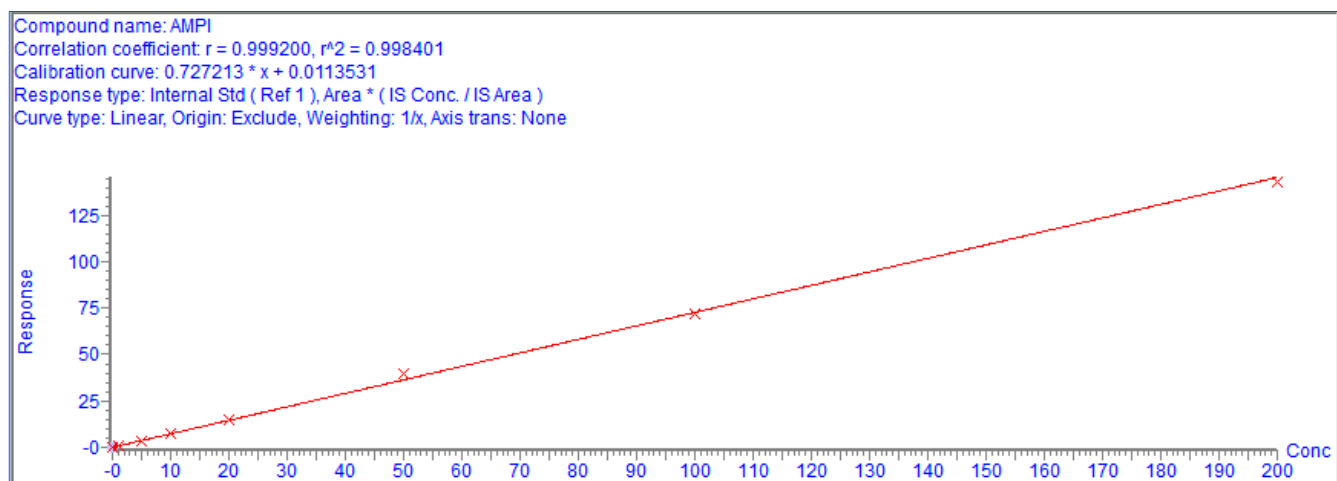


Figure S26-S33: Method validation-Linearity of target antibiotics

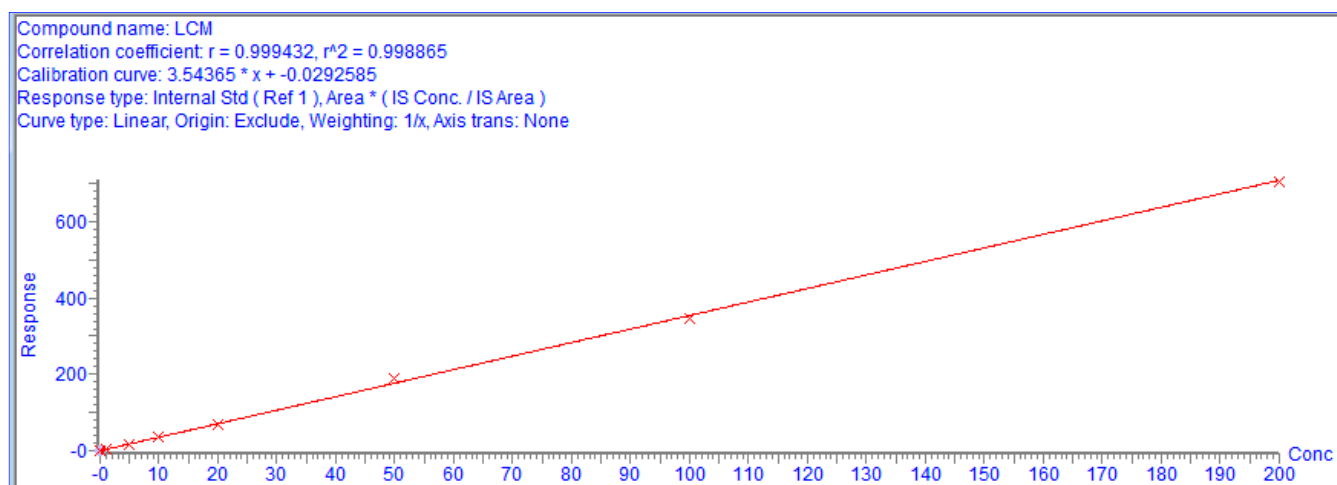
S26. Linearity of amoxicilline.



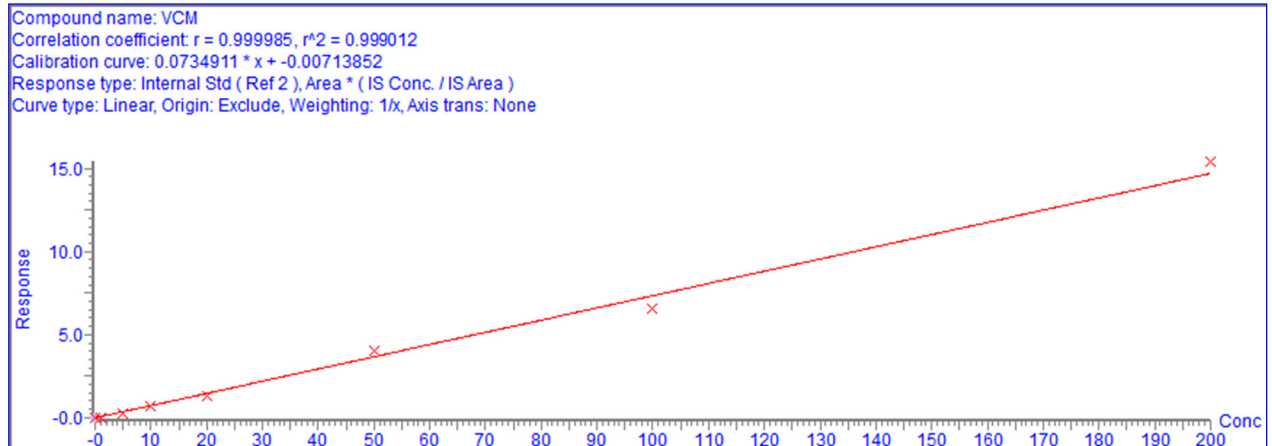
S27. Linearity of ampicilline.



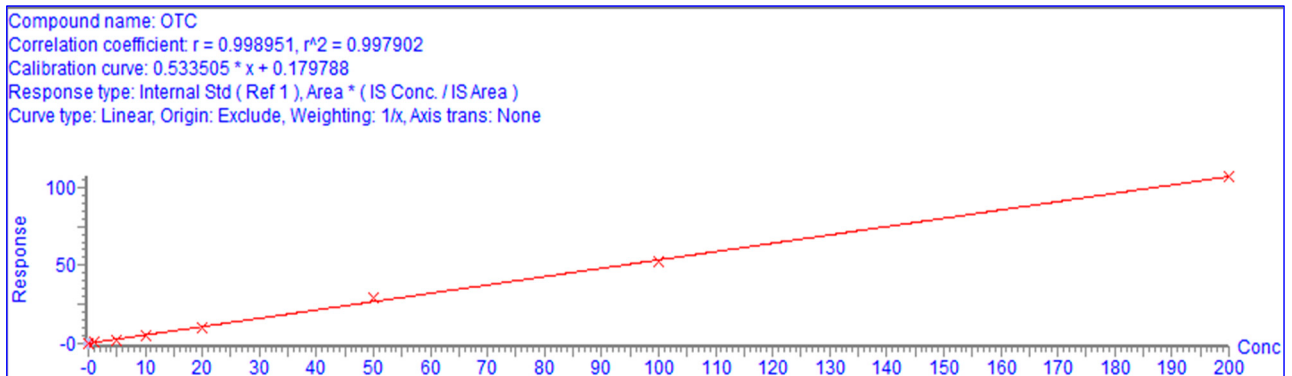
S28. Linearity of lincomycin (LCM).



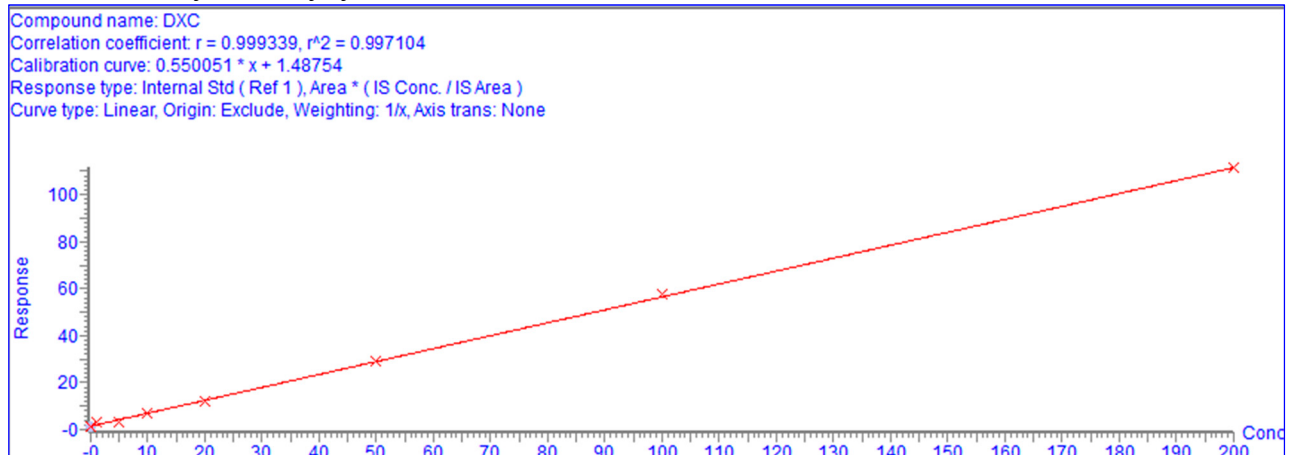
S29. Linearity of vancomycin (VCM).



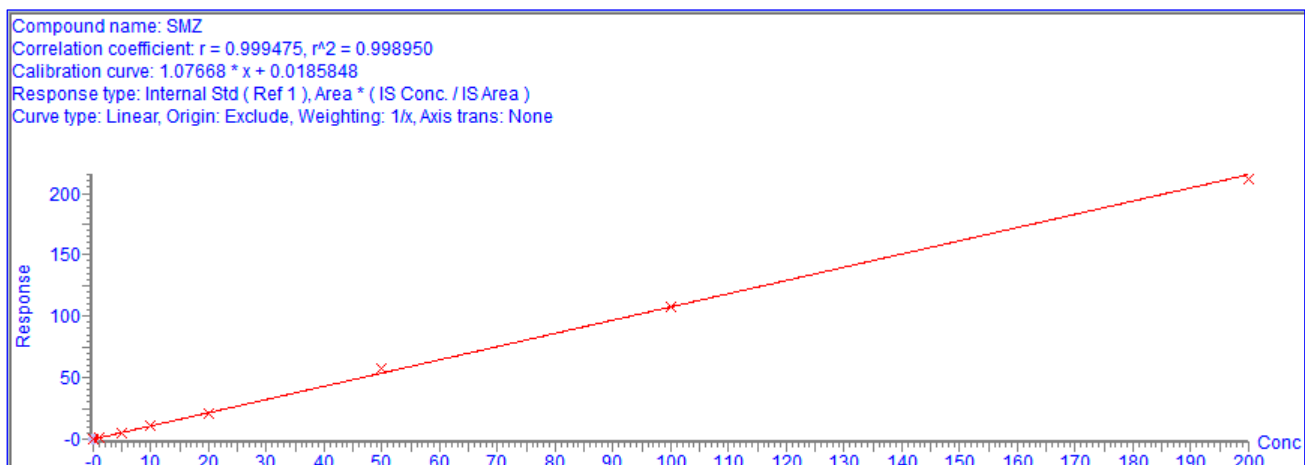
S30. Linearity of oxytetracycline (OTC).



S31. Linearity of doxycycline (DXC).



S32. Linearity of sulfamethazine (SMZ).



S33. Linearity of sulfamethoxazole (SMZX).

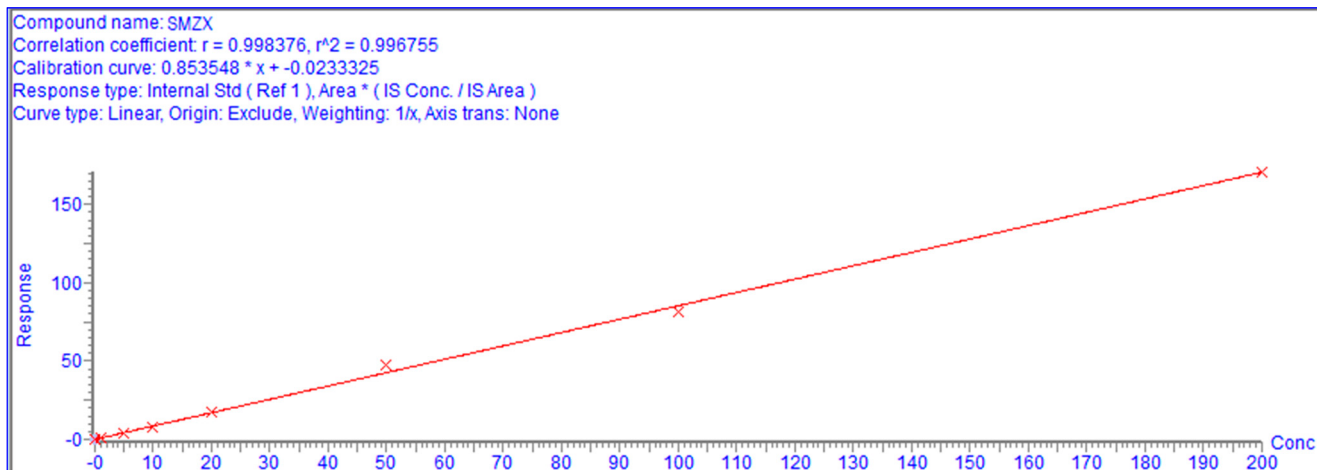
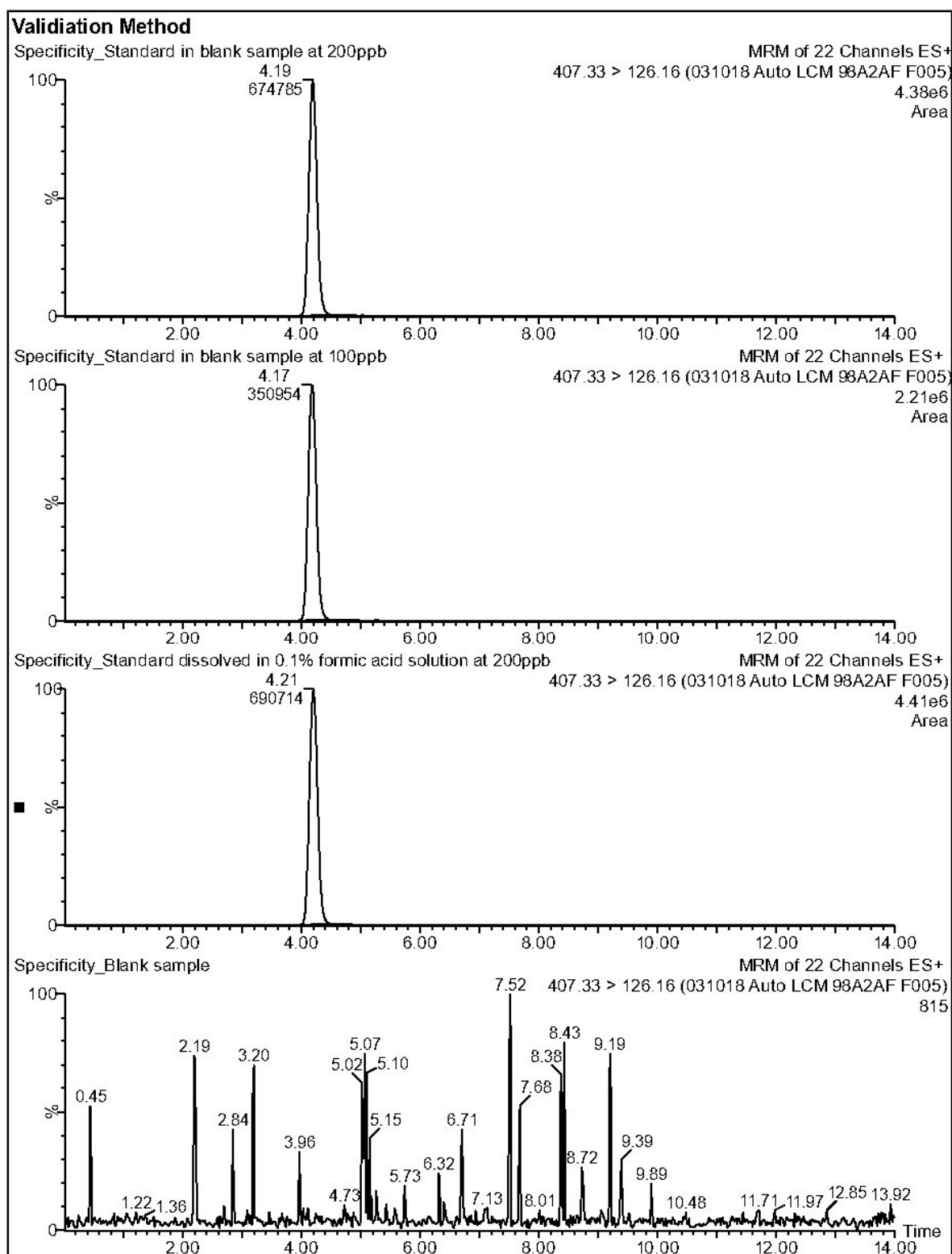
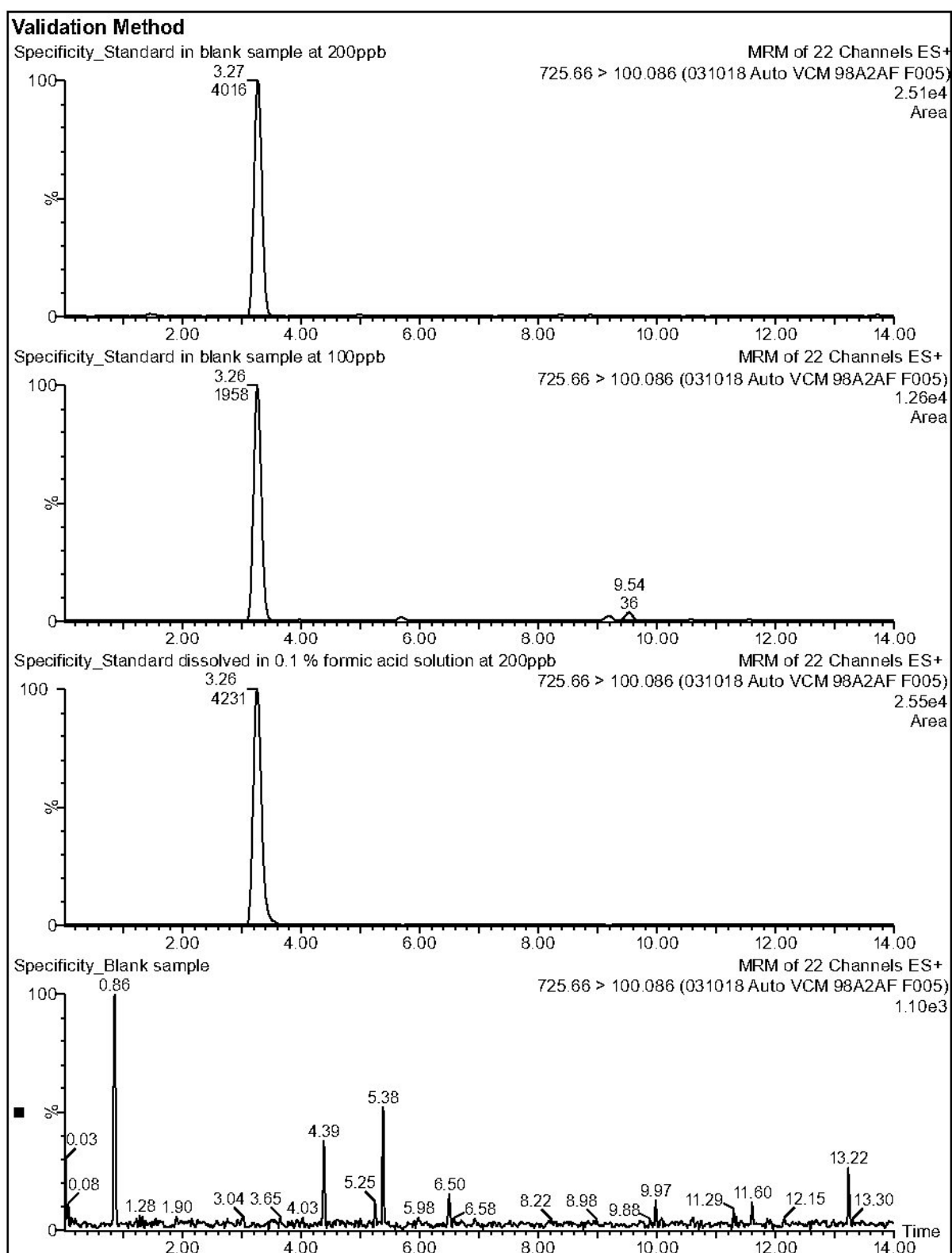


Figure S34-S36: Method validation- LC-MS/MS chromatograms for specificity of target antibiotics.

S34. LC-MS/MS chromatogram of specificity of lincomycin (LCM).



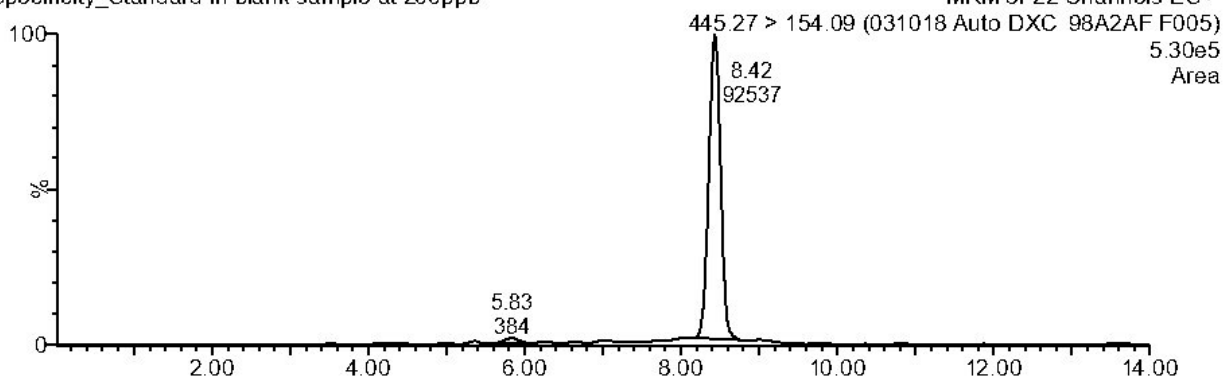
S35. LC-MS/MS chromatogram of specificity of vancomycin.



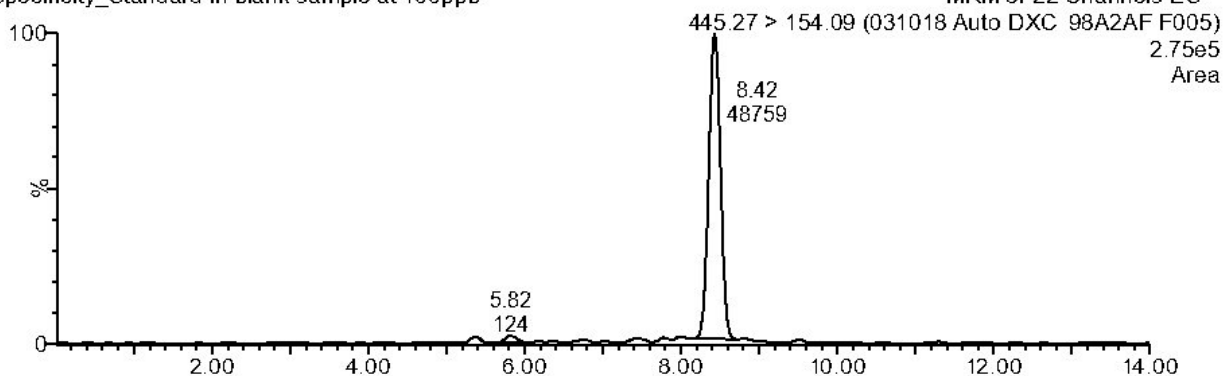
S36. LC-MS/MS chromatogram of specificity of doxycycline (DXC).

Validation Method

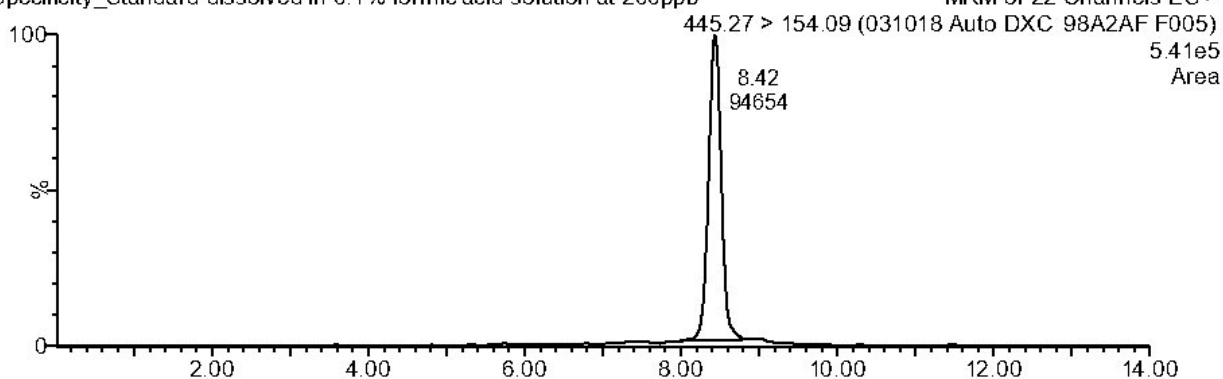
Specificity_Standard in blank sample at 200ppb



Specificity_Standard in blank sample at 100ppb



Specificity_Standard dissolved in 0.1% formic acid solution at 200ppb



Specificity_Blank sample

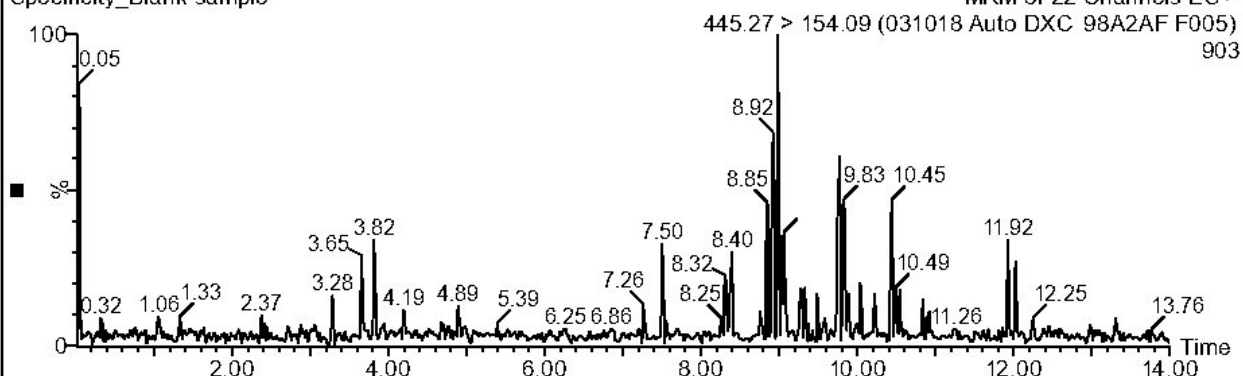
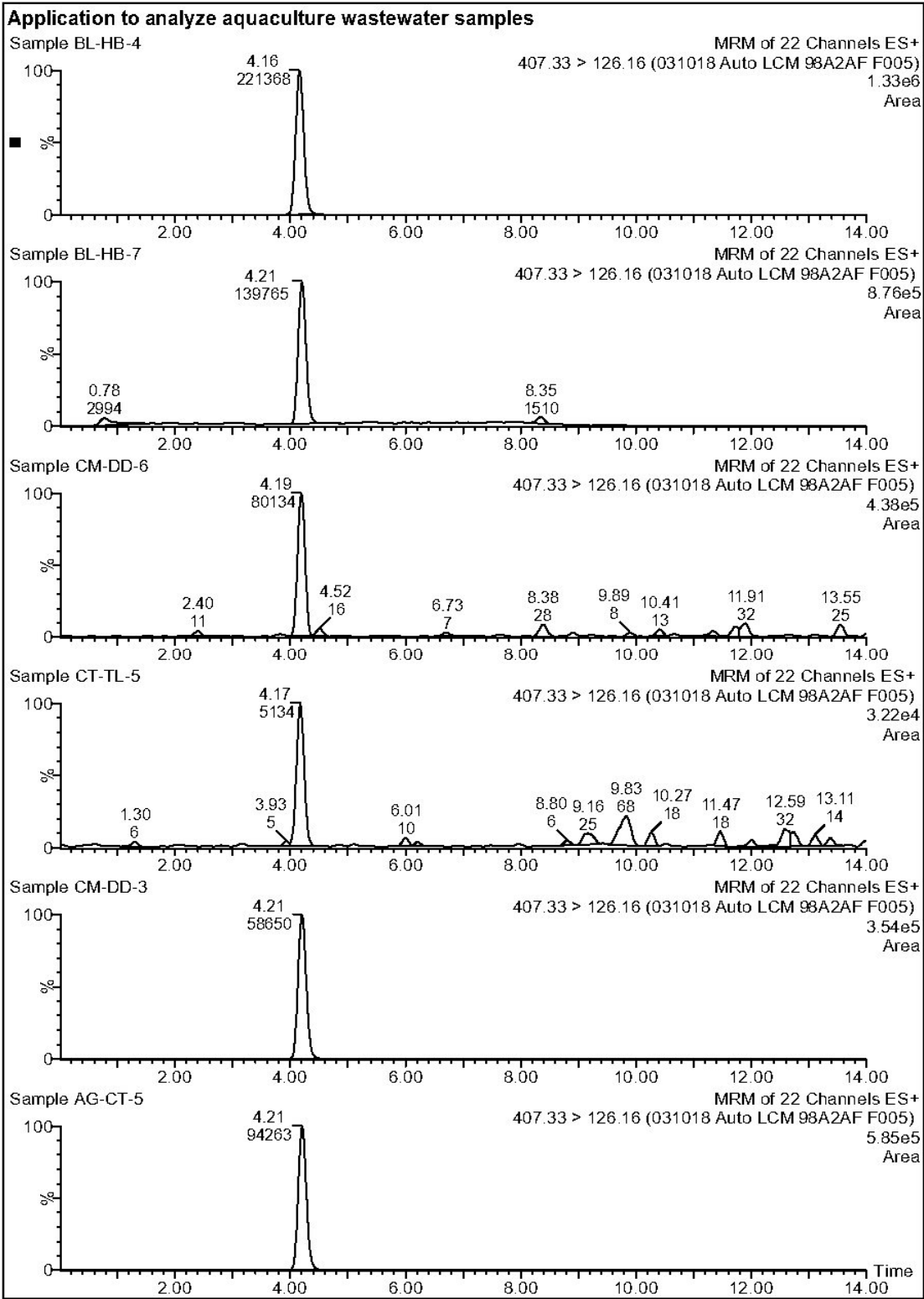
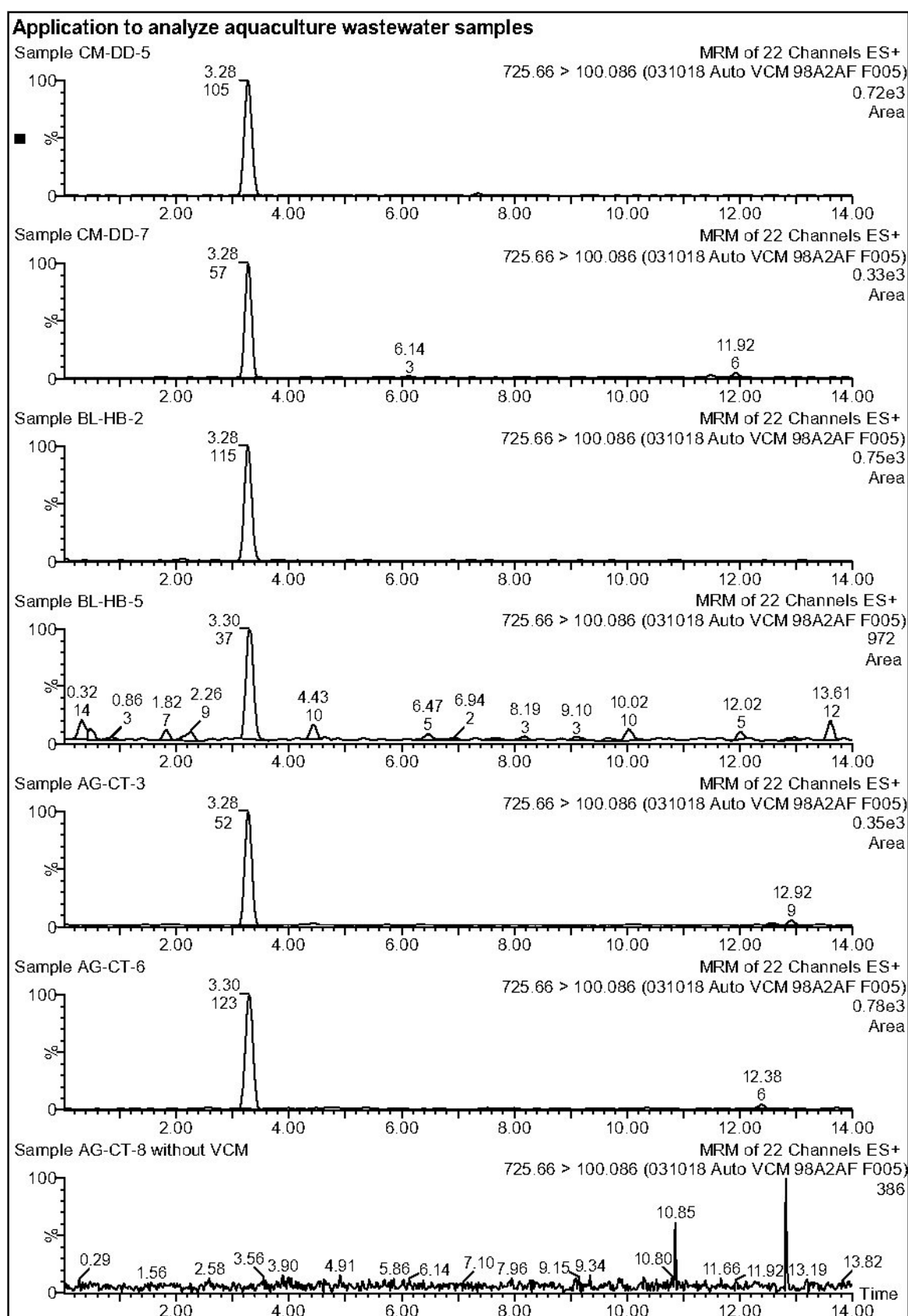


Figure S37-S41: LC-MS/MS chromatograms of analyzing aquaculture and river/canal water samples.

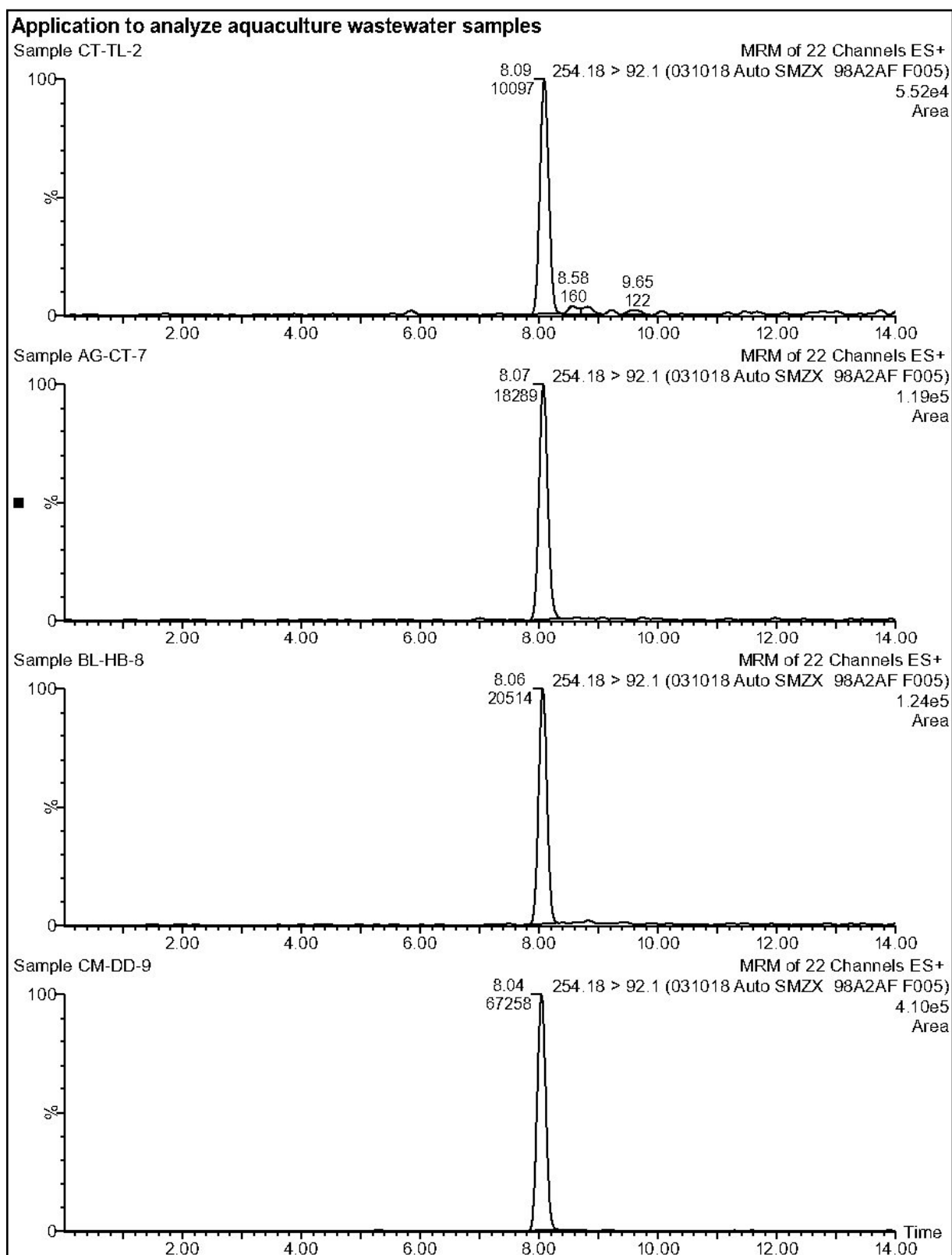
S37. LC-MS/MS chromatogram of lincomycin detection in aquaculture wastewater samples.



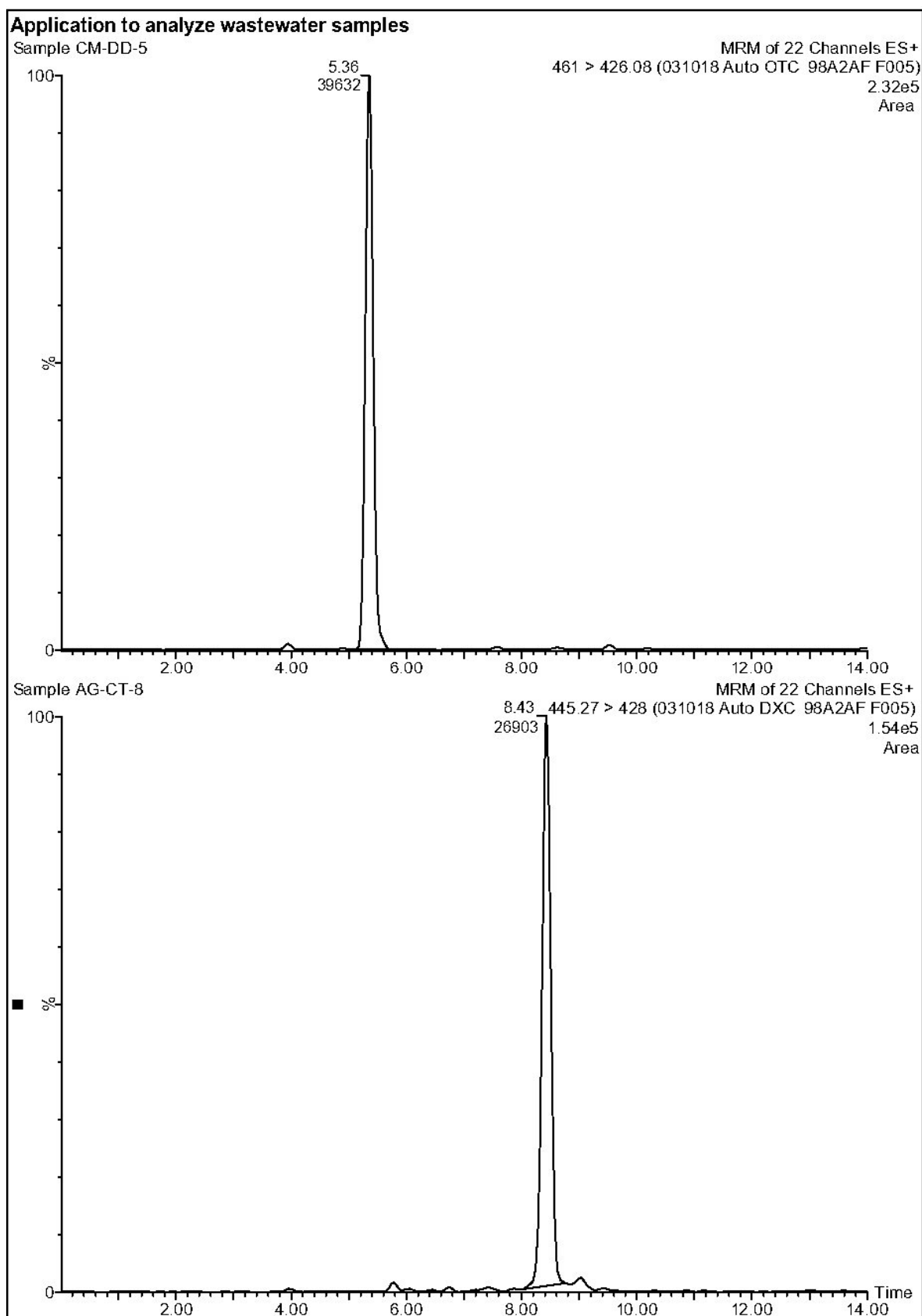
S38. LC-MS/MS chromatogram of vancomycin (VCM) detection in aquaculture wastewater samples.



S39. LC-MS/MS chromatogram of sulfamethoxazole (SMZX) detection in aquaculture wastewater samples.



S40. LC-MS/MS chromatograms show the high concentrations of oxytetracycline and doxycycline in aquaculture wastewater samples.



S41. LC-MS/MS chromatogram of doxycycline detection in river/canal water samples.

