

Table S1. An overview of currently published analytical methods for caspofungin determination

Method (Year)	IS	Standard curves (mg/L)	Mobile Phase	Column	Flow Rate (mL/min)	Run time (min)	Reference
LC-MS/MS (2006)	Caspofungin isotope	0.04-20	Mobile phase A: 10mM ammonium acetate in H ₂ O containing 1% aceticacid; Mobile phase B: 1% aceticacid in MeCN. Mobile-phase system (A:B): (75:25-30:70) (0-5.5min); (30:70-2:98) (5.5-10.0min); (2:98-75:25) (10.0-15.0min)	RP8 analytical column (2.1×30mm, 3.5µm)	0.4	15	[11]
UPLC-MS/MS (2010)	Deuterated isotopic	0.01-50	Mobile phase A: 10 mM ammonium formate in ultrapure water plus 0.1% FA; Mobile phase B: acetonitrile plus 0.1% FA	Acquity UPLC C ₁₈ analytical column (2.1× 30mm, 1.7µm)	0.5	7	[12]
LC-MS/MS (2010)	Caspofungin derivate	0.108-5.4	Mobile phase A: water with 0.1% formic acid; Mobile phase B: Acetonitrile. Mobile-phase system (A:B): (50:50-25:75) (0-3.2min); (25:75-10:90) (3.2-3.5min); (10:90-10:90) (3.5-6.8min); (10:90-50:50) (6.8-8.0min)	BetaBasic C ₄ (100× 3.0 mm)	0.25	8	[13]
LC-MS/MS (2013)	Anidulafungin	0.1-20	Mobile phase A: an aqueous buffer (pH 3.5) containing ammonium acetate (5 g/L), acetic acid (35 mg/L), and trifluoroacetic anhydride (2 mL/L) in water; Mobile phase B: Water; Mobile phase C: acetonitrile	BetaBasic C ₄ (100× 3.0 mm)	0.25	10	[14]
LC-LC/ ESI-MS/MS (2004)	ND	0.2-20	pure water acetonitrile	Vertex Eurospher 100 Diol (30×4mm, 7µm); Vertex	0.8 0.4	30	[15]

UHPLC-MS/MS (2012)	Anidulafungin	0.06-30	Mobile phase A: 10mM ammonium formate with 0.1% FA; Mobile phase B: MeCN with 0.1% FA	Eurospher 100 CN (30× 4mm, 7um) C ₁₈ column (2.1 × 30 mm, 1.7 um)	0.4	7	[16]
HPLC (2006)	Clarithromycin	0.07-35	A solution of anhydrous citric acid (0.05M), adjusted to pH 6.3 with sodiumhydroxide, and acetonitrile in a 67:33 volume	LiChroCART CN, (250×4.0mm, 5um)	1.0	10	[17]