Electronic Supplementary Material (ESI) for Analyst.

Supplementary material

Development of laser ablation dielectric barrier discharge optical emission spectrometry (LA-DBD-OES) for direct determination of sulphur and chloride in condensed phase and its application in pharmaceutical analysis

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Table S1. Interferences of dopant ions on intensities of S and Cl of the analytes.

Sample	**Maximum emission variations of S (I) 675.7 nm or Cl (II) 479.3 nm**									
	Na^+	Ca^{2+}	Cu^{2+}	Zn^{2+}	K^+	Mn^{2+}	Fe^{3+}	SO_4^{2-}	Cl^-	Br^-
CAP	5.52%	-6.52%	-1.56%	4.01%	3.67%	-3.16%	-8.78%	1.76%	8.11%	4.20%
DCDMH	3.35%	-6.42%	-7.00%	3.23%	-2.73%	1.18%	-2.69%	-0.68%	3.32%	-0.45%
NCS	-7.57%	-7.65%	1.91%	-1.28%	-2.80%	-6.53%	-6.53%	-6.77%	5.61%	-2.55%
SDZ	-1.37%	0.73%	-9.13%	-7.86%	-1.81%	-3.20%	-2.53%	3.54%	-8.00%	0.90%
BSA	5.17%	0.73%	-1.44%	-6.65%	-2.67%	-6.44%	8.55%	2.95%	-1.00%	-3.78%

Table S2. Cl and S emissions of CAP and SDZ in commercial pharmaceutical tablets at different sites on tablet surfaces.

Band		**Intensity**						
		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	RSD
CAP	Cl (II) 479.3 nm	2674.80	2453.92	2706.35	2623.83	2871.4	2191.78	9.1%
	Cl (II) 485.3 nm	3813.17	3723.36	3910.26	3876.27	3878.7	3048.59	8.9%
	Cl (II) 492.0 nm	3274.32	3257.33	3291.31	3143.25	3206.36	2652.95	7.8%
	Cl (II) 507.5 nm	3296.17	3058.3	3288.89	3169.95	3172.38	2703.93	7.1%
	Cl (II) 521.9 nm	3616.56	3458.79	3696.66	3504.91	3497.63	3143.25	5.4%
SDZ	S (I) 675.7 nm	4633.56	4525.31	4456.37	4530.65	4482.59	4647.64	1.7%
	S (II) 677.6 nm	4123.37	4015.11	4018.51	4219.97	4077.25	4264.63	2.5%

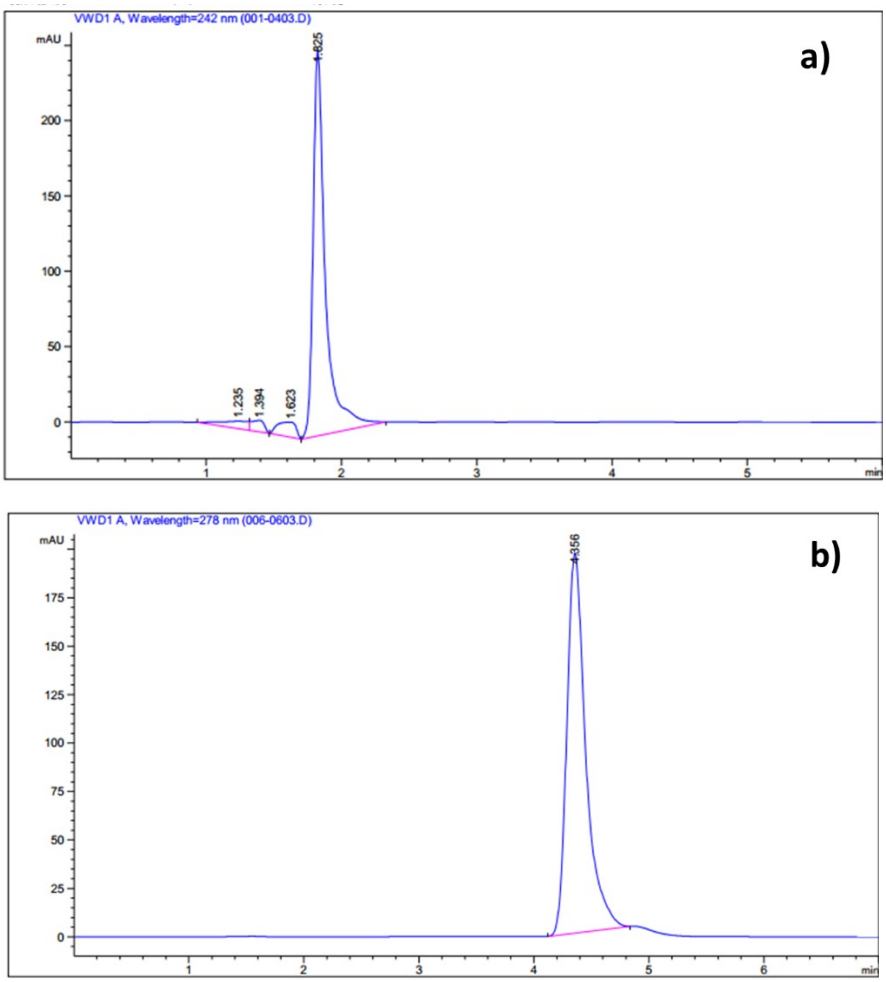

Figure S1. Chromatographic spectra of a) SDZ and b) CAP. Injection amounts were1 µg for SDZ and CAP.

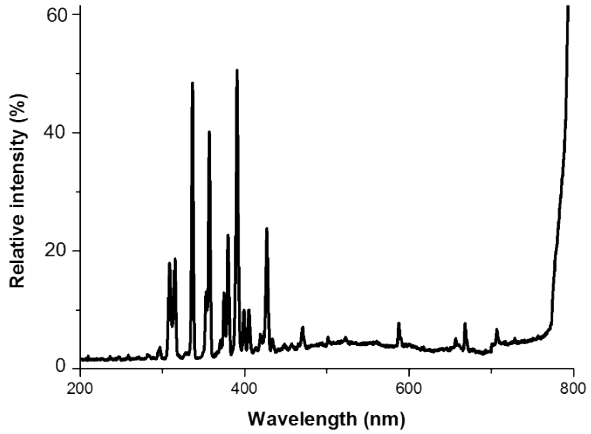

Figure S2. Background emission spectrum of the LA-DB-OES with laser power of 1W.

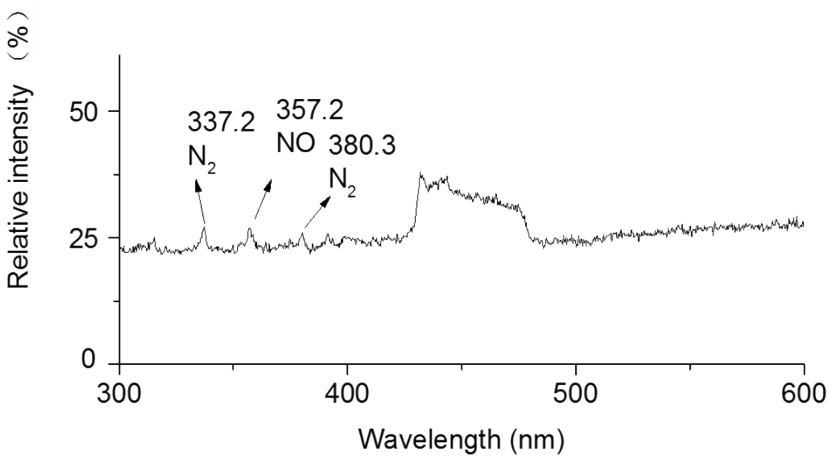

Figure S3. Emission spectrum of a 5% BSA tablet obtained with a 1W laser focused onto the sample surface.

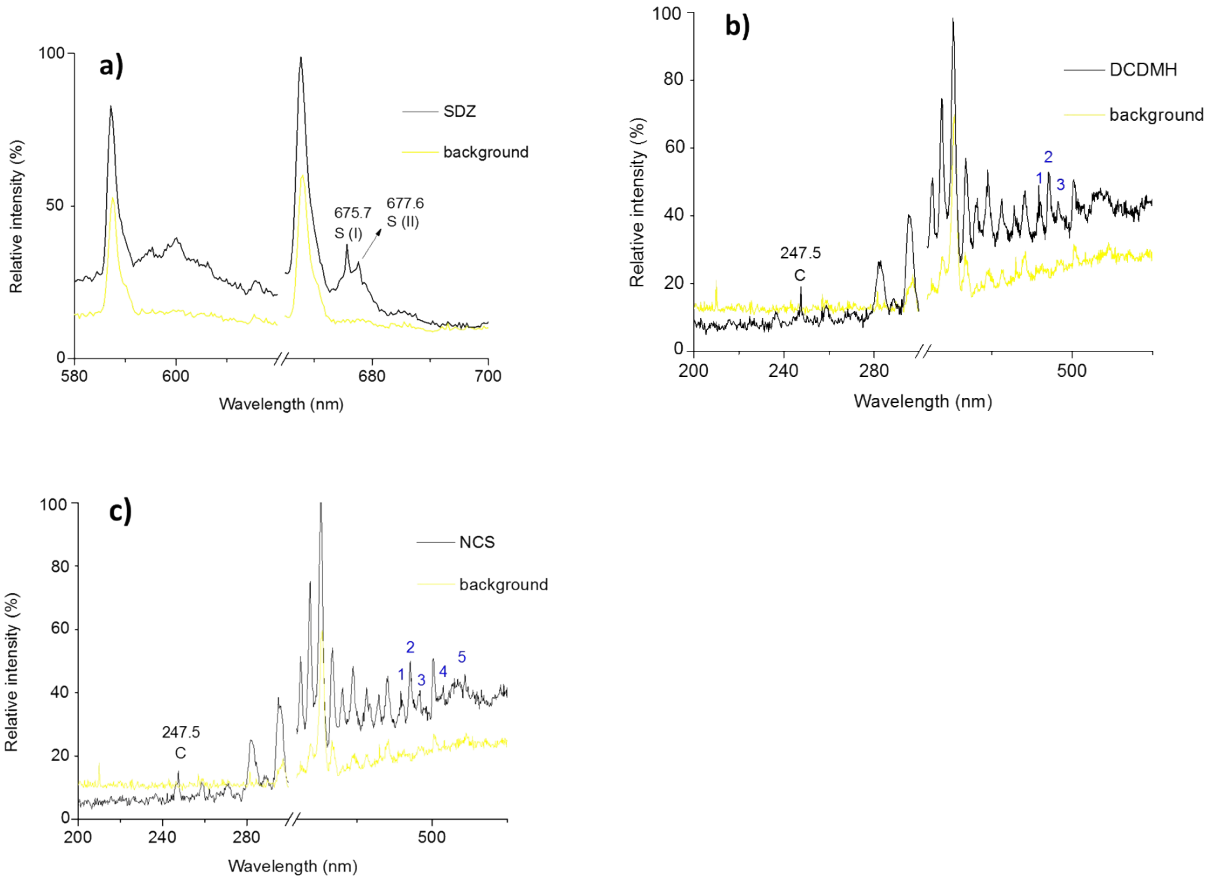

Figure S4. Spectra of a) a 5% SDZ tablet, b) a 5% DCDMH tablet and c) a 5% NCS tablet. Marked peaks 1-5 are assigned to Cl (II) emissions at 479.3, 485.3, 492.0, 507.5 and 521.9 nm, respectively.

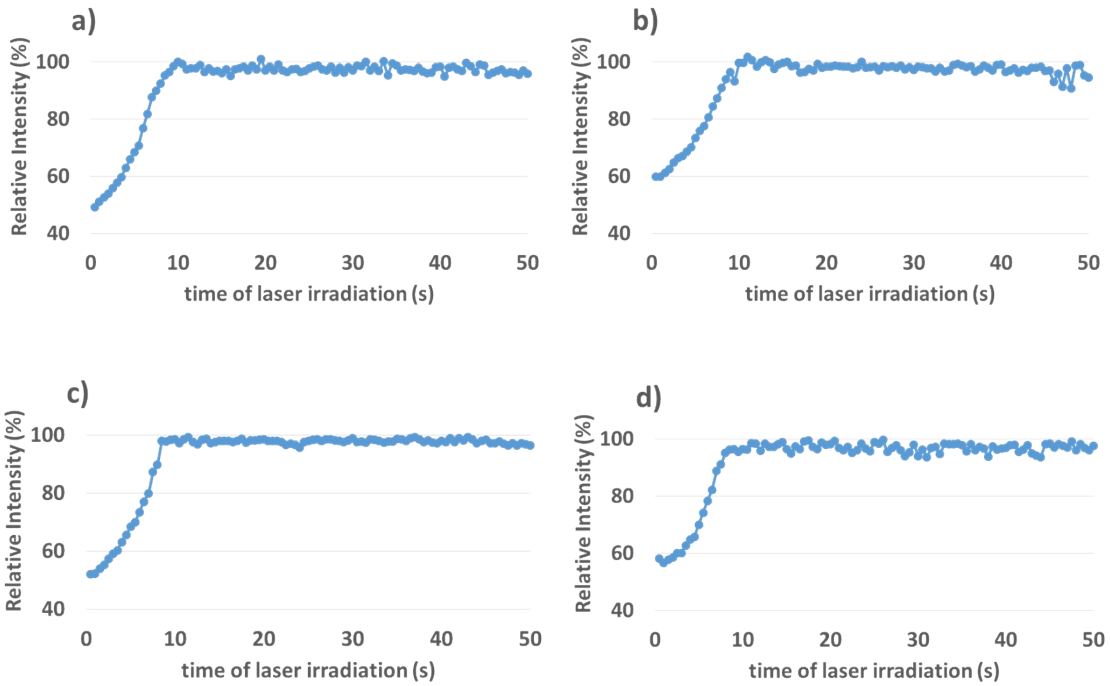

Figure S5. Variations of intensities of Cl (II) at 479.3 nm and S (I) at 675.7 nm along the laser irradiation time. Graphs a) to d) correspond to emissions from 100% tablets of DCDMH, CAP, BSA and SDZ, respectively. DCDMH and CAP were detected at laser output of 2 W while BSA and SDZ were detected with a 1W laser.

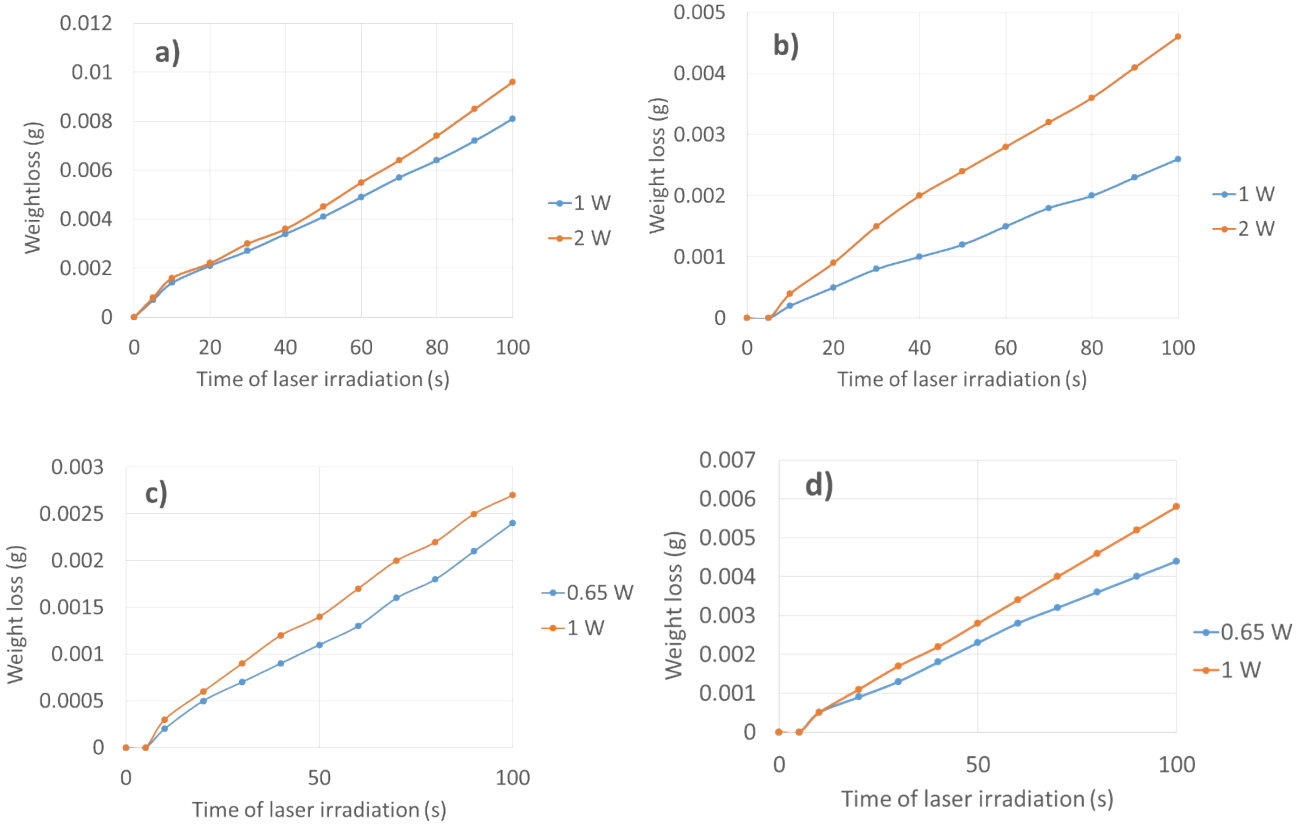

Figure S6. Amount of weight loss of a) a 100% DCDMH tablet, b) a 100% CAP tablet, c) a 100% BSA tablet and d) a 100% SDZ tablet as a function of laser irradiation time.

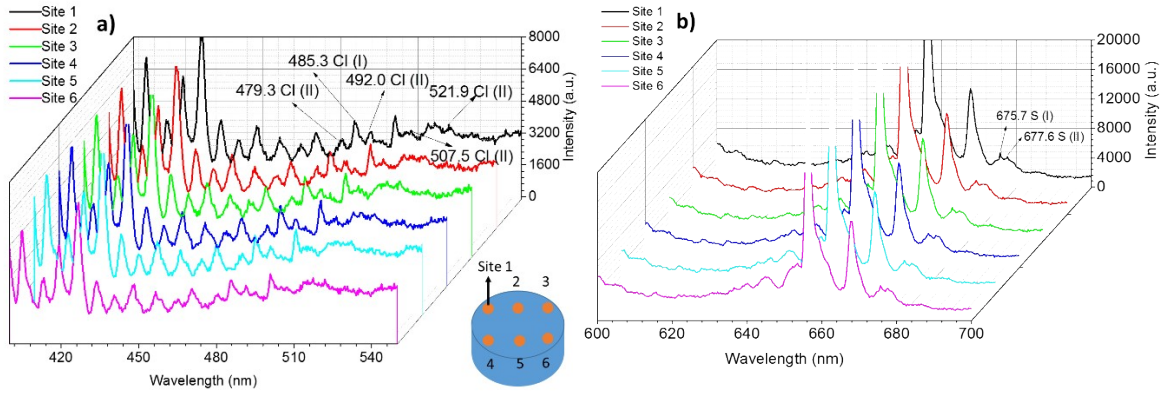

Figure S7. Emission spectra at different sites on surfaces of a) a commercial CAP tablet and b) a commercial SDZ tablet.

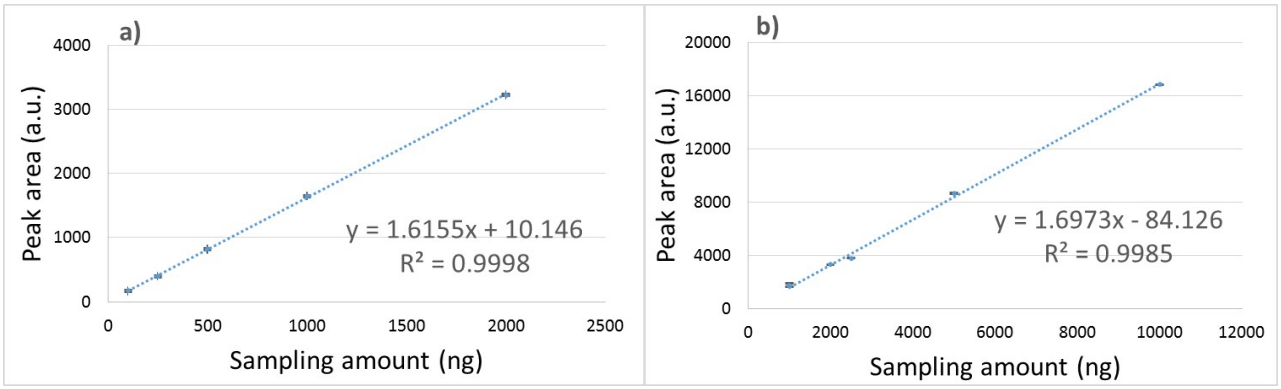

Figure S8. Calibration curves of a) SDZ and b) CAP measured with HPLC. Each data point was measured in triplicate.

From the calibration equation of SDZ, one can determine the sampling amount of SDZ as

$$x=(y-10.146)/1.6155,$$

where x represents the sampling amount of SDZ with an injection volume of 10 µL and y represents the peak area of SDZ. Therefore, the percentage composition of SDZ (w) in a commercial tablet can be calculated as

$$\omega=C_{det}/C_{pre},$$

where C_{det} is the detected concentration of SDZ as x/10 µg/mL and C_{prep} is the concentration of SDZ tablet solution prepared as 40 µg/mL. Given the weight of the commercial SDZ tablet α, the actual active ingredient content (σ) can be estimated as

$$\sigma=\alpha\times\omega$$

The actual CAP content in a commercial tablet was determined in a similar way.