Electronic Supplementary Material (ESI) for Analytical Methods.

SUPPLEMENTARY MATERIAL

Rapid evaporative ionization mass spectrometry (REIMS) combined with chemometrics for real-time beer analysis

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Table S1. Information about samples.

Sample code	Brand code	Type	Storage	Origin country
ALM	1	Premium	Aluminium can	Brazil
AMS	2	Premium	Aluminium can	Brazil
ATO	3	Standard	Glass bottle	Brazil
ATS	4	Standard	Aluminium can	Brazil
BVR	5	Standard	Aluminium can	Brazil
BOH	6	Premium	Aluminium can	Brazil
BCL	7	Standard	Aluminium can	Brazil
BCG	8	Standard	Glass bottle	Brazil
BEL	9	Premium	Glass bottle	Brazil
BEW	10	Standard	Glass bottle	Brazil
BUD	11	Standard	Glass bottle	Brazil
CAR	12	Standard	Aluminium can	Brazil
COL	13	Standard	Aluminium can	Brazil
COR	14	Standard	Glass bottle	Mexico
EAI	15	Premium	Glass bottle	Brazil
EPA	16	Premium	Aluminium can	Brazil
EPI	17	Premium	Aluminium can	Brazil
EWB	18	Standard	Glass bottle	Brazil
EWE	19	Standard	Glass bottle	Brazil
EST	20	Standard	Glass bottle	Spain
HNK	21	Premium	Glass bottle	Brazil
IMP	22	Premium	Glass bottle	Brazil
ITA	23	Standard	Glass bottle	Brazil
ITM	24	Standard	Aluminium can	Brazil
PTR	25	Standard	Aluminium can	Brazil
PTO	26	Premium	Glass bottle	Brazil
SCH	27	Standard	Aluminium can	Brazil
SEM	28	Premium	Glass bottle	Brazil
SKP	29	Premium	Aluminium can	Brazil
SKO	30	Standard	Aluminium can	Brazil
SOL	31	Standard	Aluminium can	Brazil
STA	32	Standard	Glass bottle	Brazil

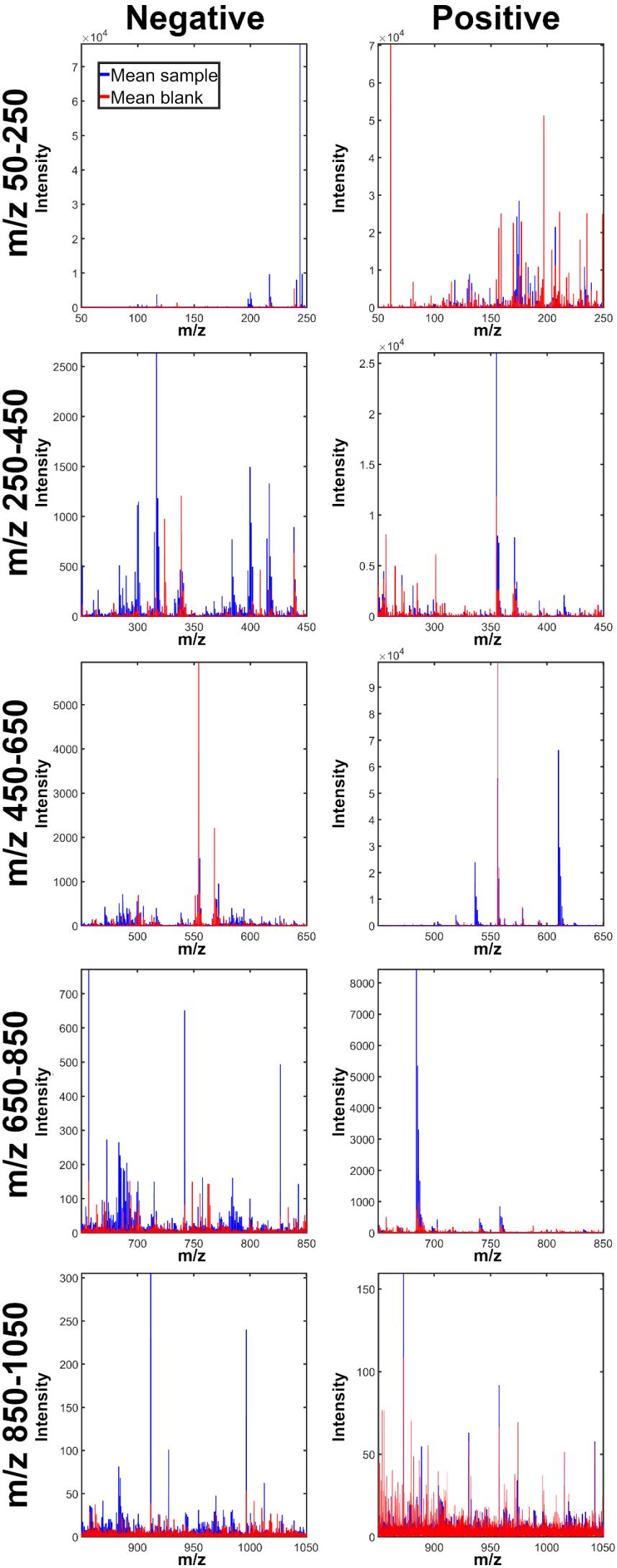

Figure S1. Comparison between mean spectra and mean blank in different spectral ranges in both modes.

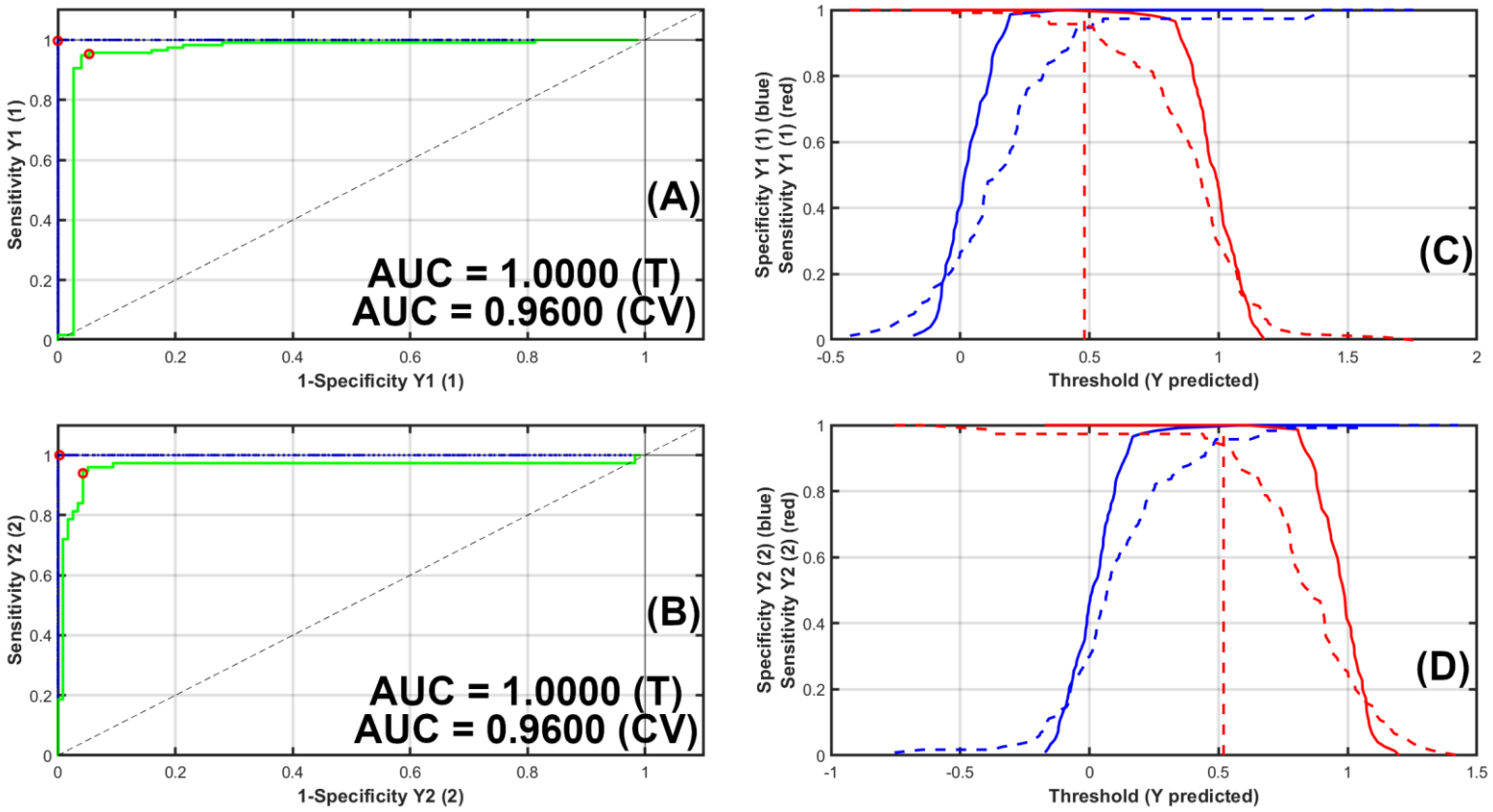

Figure S2. Type model: ROC curves of (a) standard American lagers and (b) premium American lagers, being blue lines of training step (T) and green lines of cross-validation (CV). Estimated responses according to threshold of (c) standard American lagers and (d) premium American lagers, being solid lines of training step, dashed lines of cross-validation, blue lines of specificity and red lines of sensitivity.

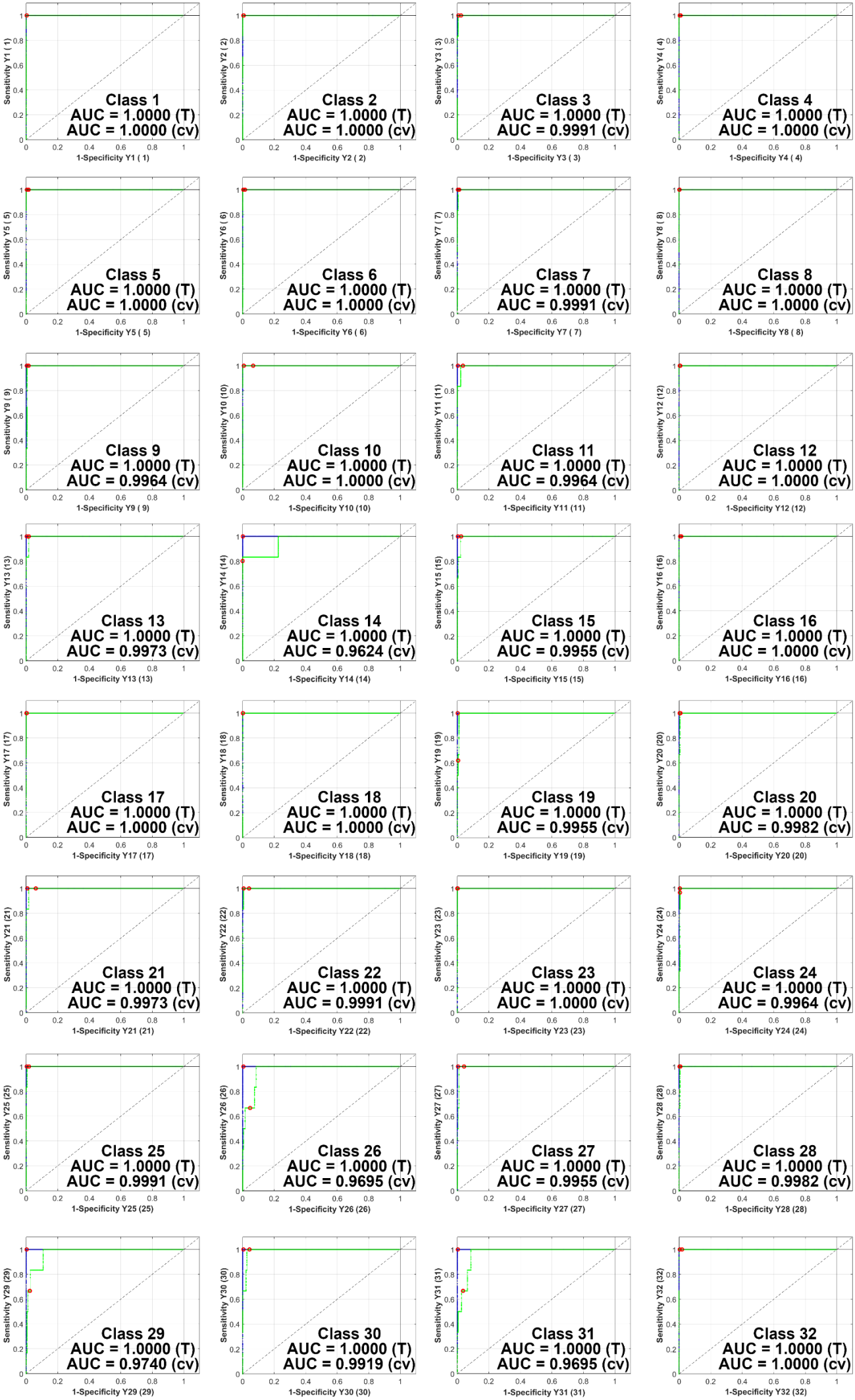

Figure S3. Brand model: ROC curves of each class, being blue lines of training step (T) and green lines of cross-validation (CV).

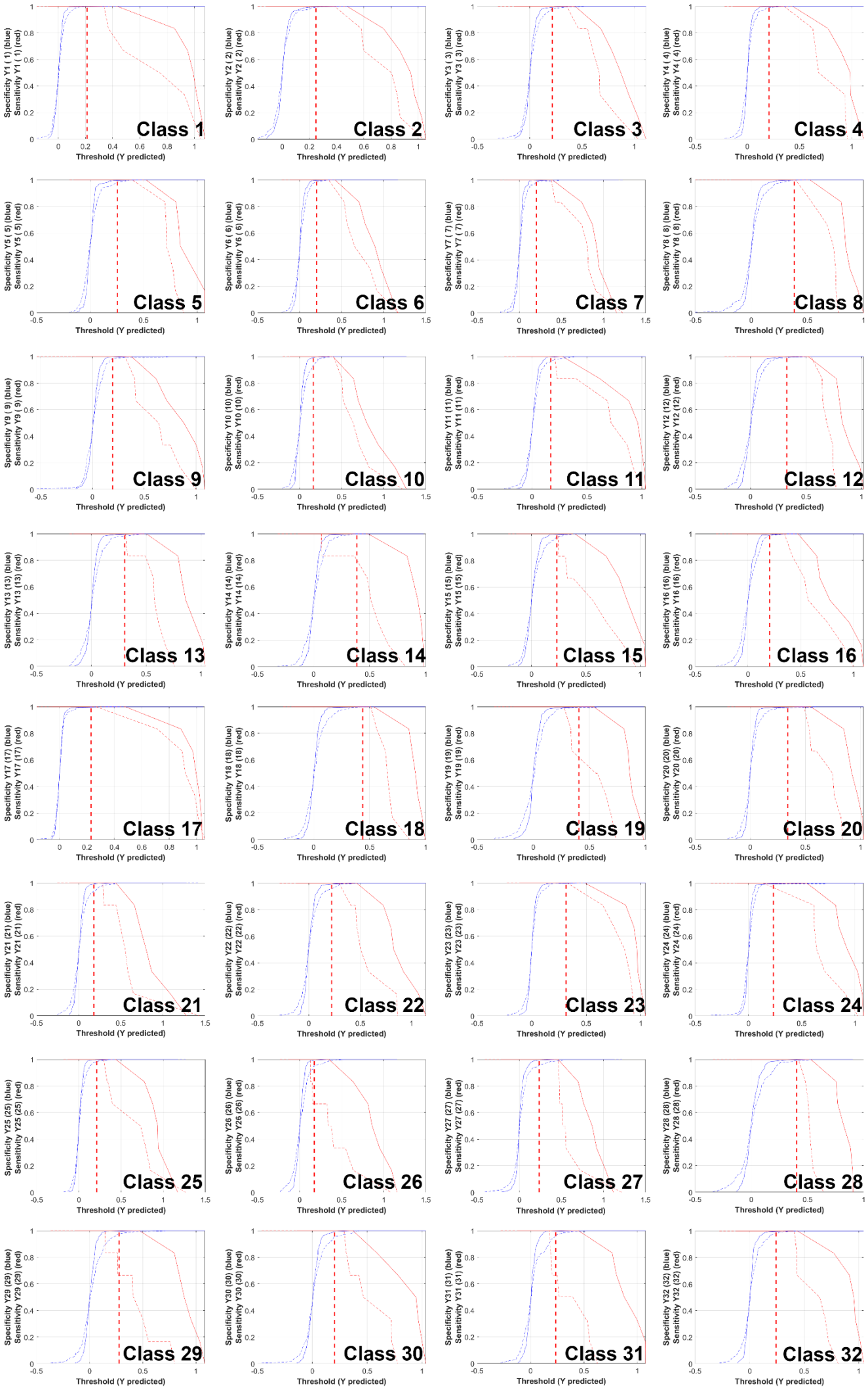

Figure S4. Brand model: Estimated responses according to threshold of each class, being solid lines of training step, dashed lines of cross-validation, blue lines of specificity and red lines of sensitivity.

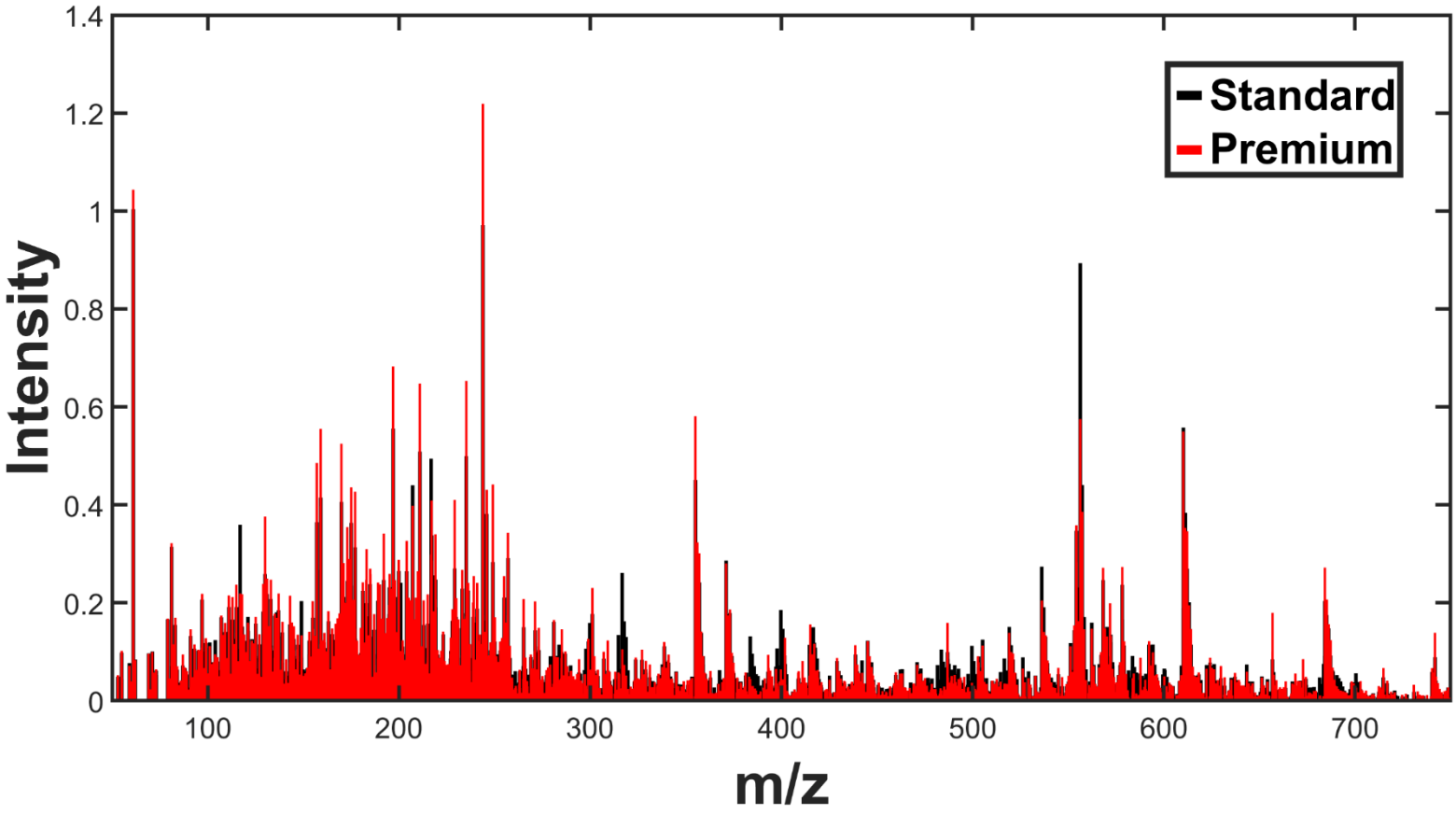

Figure S5. Comparison between mean combined spectra of standard American lagers and premium American lagers.

Table S2. Assignment of the most intense VIP scores of both models for positive ionization mode.

Positive						
Adduct type	Accurate mass	Exact mass	Empirical formula	DBE	Error (ppm)	Model
$[M+H]^+$	61.0637	61.0640	CH_7N_3	0	-4.87	Brand
$[M+Na]^+$	173.0164	173.0174	$C_3H_6N_2O_5Na$	1.5	-6.01	Brand
$[M+Na]^+$	175.0374	175.0371	$C_8H_8O_3Na$	4.5	1.64	Brand
$[M+H]^+$	177.0784	177.0790	$C_{10}H_{11}NO_2$	6	-3.27	Brand
$[M+H]^+$		177.0776	$C_8H_9N_4O$	6.5	4.31	
$[M+Na]^+$		177.0766	$C_8H_{12}NO_2Na$	3	10.32	
$[M+H]^+$	183.0412	183.0406	$C_7H_7N_2O_4$	5.5	3.38	Both
$[M+Na]^+$	185.0421	185.0426	$C_6H_{10}O_5Na$	1.5	-2.66	Both
-	196.9477	-	-	-	-	Both
$[M+Na]^+$	207.1725	207.1725	$C_{12}H_{24}ONa$	0.5	0	Brand
$[M+H]^+$		207.1735	$C_{12}H_{21}N_3$	4	-5.06	
$[M+Na]^+$	229.1429	229.1429	$C_{11}H_{18}N_4Na$	4.5	0	Brand
$[M+H]^+$		229.1426	$C_{10}H_{19}N_3O_3$	3	1.13	
$[M+H]^+$		229.1440	$C_{12}H_{21}O_4$	2.5	-4.73	
-	233.0847	-	-	-	-	Brand
$[M+H]^+$	235.2058	235.2062	$C_{16}H_{27}O$	3.5	-1.66	Both
$[M+H]^+$		235.2048	$C_{14}H_{25}N_3$	4	4.05	
$[M+Na]^+$		235.2038	$C_{14}H_{28}ONa$	0.5	8.57	
$[M+H]^+$	249.1123	249.1127	$C_{14}H_{17}O_4$	6.5	-1.54	Both
$[M+Na]^+$		249.1130	$C_{15}H_{16}NONa$	8	-0.66	
$[M+Na]^+$	301.1368	301.1376	$C_{11}H_{22}N_2O_6Na$	1.5	-2.51	Type
$[M+H]^+$		301.1386	$C_{11}H_{19}N_5O_5$	5	-6.04	
$[M+Na]^+$	355.0622	355.0655	$C_{14}H_{12}N_4O_6Na$	10.5	-9.16	Brand
-	536.1676	-	-	-	-	Both
$[M+H]^+$	556.2771	556.2771	$C_{28}H_{38}N_5O_7$	12.5	0	Both
$[M+Na]^+$	557.2775	557.2753	$C_{32}H_{40}NO_6Na$	13	3.89	Brand
$[M+Na]^+$		557.2740	$C_{30}H_{38}N_4O_5Na$	13.5	6.30	
-	610.1825	-	-	-	-	Both
-	611.1830	-	-	-	-	Brand
-	612.1834	-	-	-	-	Both

Table S3. Assignment of the most intense VIP scores of both models for negative ionization mode.

Negative						
Adduct type	Accurate mass	Exact mass	Empirical formula	DBE	Error (ppm)	Model
-	134.8950	-	-	-	-	Brand
-	200.8644	-	-	-	-	Brand
-	216.8515	-	-	-	-	Brand
-	238.8413	-	-	-	-	Brand
-	240.9022	-	-	-	-	Brand
-	243.9035	-	-	-	-	Both
$[M+H]^+$	554.2615	554.2615	$C_{28}H_{36}N_5O_7$	13.5	0	Brand