

### Supplementary Data S2 – Validation sample set compositions and classification results

| sample | Nominal Class | Sample mixture composition (% v/v)                         | SIMCA | SVM |
|--------|---------------|--|-------|-----|
| 1      |               | PN3  | (2)   | 1   |
| 2      |               | 0.25 PBS + 0.75 PN3  | 1     | 1   |
| 3      |               | PSP  | 1     | 1   |
| 4      |               | PN5  | 1     | 1   |
| 5      |               | 0.50 PN1 + 0.50 PN2  | (2)   | (4) |
| 6      |               | 0.50 PN2 + 0.50 PN3  | 1     | 1   |
| 7      | 1             | 0.75 PN2 + 0.25 PN3  | 1     | 1   |
| 8      |               | 0.75 PN3 + 0.25 PN2  | 1     | 1   |
| 9      |               | 0.33 PN1 + 0.33 PN2 + 0.33 PN3                             | 1     | 1   |
| 10     |               | 0.15 PN2 + 0.55 PN3 + 0.30 PBS                             | 1     | 1   |
| 11     |               | 0.50 PN4 + 0.50 PN5  | 1     | 1   |
| 12     |               | 0.50 PN4 + 0.50 PN2 *                                      | 1     | 1   |
| 13     |               | 0.50 PN5 + 0.50 PN2 *                                      | 1     | 1   |
| 14     |               | 0.90 PN3 + 0.10 NH   | 2     | 2   |
| 15     |               | 0.90 (0.25 PBS + 0.75 PN3) + 0.10 NH                       | 2     | 2   |
| 16     |               | 0.90 PN5 + 0.10 NH   | 2     | 2   |
| 17     |               | 0.90 PSP + 0.10 NH   | 2     | 2   |
| 18     |               | 0.85 PN3 + 0.15 NH   | 2     | 2   |
| 19     |               | 0.85 (0.25 PBS + 0.75 PN3) + 0.15 NH                       | 2     | 2   |
| 20     |               | 0.85 PN5 + 0.15 NH   | 2     | 2   |
| 21     |               | 0.85 PSP + 0.15 NH   | 2     | 2   |
| 22     |               | 0.85 (0.5 PN1 + 0.5 PN2) + 0.15 NH                         | 2     | 2   |
| 23     |               | 0.85 (0.5 PN2 + 0.5 PN3) + 0.15 NH                         | 2     | 2   |
| 24     | 2             | 0.85 (0.75 PN2 + 0.25 PN3) + 0.15 NH                       | 2     | 2   |
| 25     |               | 0.85 (0.75 PN3 + 0.25 PN2) + 0.15 NH                       | 2     | 2   |
| 26     |               | 0.85 (0.33 PN1 + 0.33 PN2 + 0.33 PN3) + 0.15 NH            | 2     | (3) |
| 27     |               | 0.85 (0.15 PN2 + 0.55 PN3 + 0.30 PBS) + 0.15 NH            | 2     | 2   |
| 28     |               | 0.85 (0.5 PN4 + 0.5 PN2) + 0.15 NH *                       | 2     | 2   |
| 29     |               | 0.85 (0.5 PN5 + 0.5 PN2) + 0.15 NH *                       | 2     | 2   |
| 30     |               | 0.93 PN4 + 0.07 NH *                                       | (1)   | 2   |
| 31     |               | 0.93 PN1 + 0.07 NH *                                       | 2     | 2   |
| 32     |               | 0.93 PN2 + 0.07 NH *                                       | 2     | 2   |
| 33     |               | 0.93 (0.25 PBS + 0.75 PN3) + 0.07 NH *                     | 2     | 2   |
| 34     |               | 0.85 PN3 + 0.1 NH + 0.05 VEG                               | 3     | 3   |
| 35     |               | 0.85 (0.25 PBS + 0.75 PN3) + 0.10 NH + 0.05 VEG            | 3     | 3   |
| 36     |               | 0.80 PN3 + 0.15 NH + 0.05 VEG                              | 3     | 3   |
| 37     |               | 0.80 (0.25 PBS + 0.75 PN3) + 0.15 NH + 0.05 VEG            | 3     | 3   |
| 38     |               | 0.80 (0.5 PN1 + 0.5 PN2) + 0.15 NH + 0.05 VEG              | 3     | 3   |
| 39     | 3             | 0.80 (0.5 PN2 + 0.5 PN3) + 0.15 NH + 0.05 VEG              | 3     | 3   |
| 40     |               | 0.80 (0.75 PN2 + 0.25 PN3) + 0.15 NH + 0.05 VEG            | 3     | 3   |
| 41     |               | 0.80 (0.75 PN3 + 0.25 PN2) + 0.15 NH + 0.05 VEG            | 3     | 3   |
| 42     |               | 0.80 (0.15 PN2 + 0.55 PN3 + 0.30 PBS) + 0.15 NH + 0.05 VEG | 3     | 3   |
| 43     |               | 0.80 (0.33 PN1 + 0.33 PN2 + 0.33 PN3) + 0.15 NH + 0.05 VEG | 3     | 3   |
| 44     |               | 0.80 (0.5 PN4 + 0.5 PN2) + 0.15 NH + 0.05 VEG *            | 3     | 3   |
| 45     |               | 0.80 (0.5 PN5 + 0.5 PN2) + 0.15 NH + 0.05 VEG *            | 3     | 3   |
| 46     |               | 0.95 PN3 + 0.05 VEG  | 4     | (3) |
| 47     |               | 0.95 (0.25 PBS + 0.75 PN3) + 0.05 VEG                      | 4     | 4   |
| 48     |               | 0.95 (0.50 PN1 + 0.50 PN2) + 0.05 VEG                      | 4     | 4   |
| 49     |               | 0.95 (0.50 PN2 + 0.50 PN3) + 0.05 VEG                      | 4     | 4   |
| 50     | 4             | 0.95 (0.75 PN2 + 0.25 PN3) + 0.05 VEG                      | 4     | 4   |
| 51     |               | 0.95 (0.75 PN3 + 0.25 PN2) + 0.05 VEG                      | 4     | 4   |
| 52     |               | 0.95 (0.15 PN2 + 0.55 PN3 + 0.30 PBS) + 0.05 VEG           | 4     | 4   |
| 53     |               | 0.95 (0.33 PN1 + 0.33 PN2 + 0.33 PN3) + 0.05 VEG           | 4     | 4   |
| 54     |               | 0.95 (0.50 PN4 + 0.50 PN2) + 0.05 VEG *                    | 4     | 4   |
| 55     |               | 0.95 (0.50 PN5 + 0.50 PN2) + 0.05 VEG *                    | 4     | 4   |

where: (class) means classification don't agree with nominal class  
 \* means don't has replication in calibration sample set