Electronic supplementary information

High dilution surface-enhanced Raman spectroscopy for rapid determination of nicotine in e-liquids for electronic cigarettes

Nobuyasu Itoh*[a] and Steven E.J. Bell[b]

[a]*National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, Japan*

[b]*Innovative Molecular Materials Group, School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom*

Contents

Figure S1. Scheme of sample preparation.

Figure S2. Raman spectra of (a) propylene glycol and (b) vegetable glycerin.

Figure S3. Spectra of (a) propylene glycol and (b) vegetable glycerine mixed with colloid and aggregating agent.

Figure S4. (a) Raman and SERS spectra of tobacco flavored e-liquid containing fresh nicotine at 18 mg mL^{-1}. (b) Raman and SERS spectra of vanilla flavored e-liquid containing old nicotine at 18 mg mL^{-1}. In both SERS spectra the samples were spiked with d_4-nicotine to give a final concentration of 10 μM.

Figure S5. (a) Blank SERS spectrum of aggregated colloid showing bands of the organic stabilizing layer (b) SERS spectrum with undiluted tobacco flavoured e-liquid showing disappearance of the colloid's background signal. Samples were prepared from of 20 μL of e-liquid (or water in the blank), 180 μL of Au colloid solution and 50 μL of 0.1 M $MgSO_4$. Spectra are on the same intensity scale.

Figure S6. Photo of all e-liquids examined in this study. Numbers on vials are corresponding to those in Fig. 6 and Tables S1−S3.

Table S1. Information of e-liquids examined in this study.

Table S2. Matching factors of each e-liquid spectrum with calibration solutions.

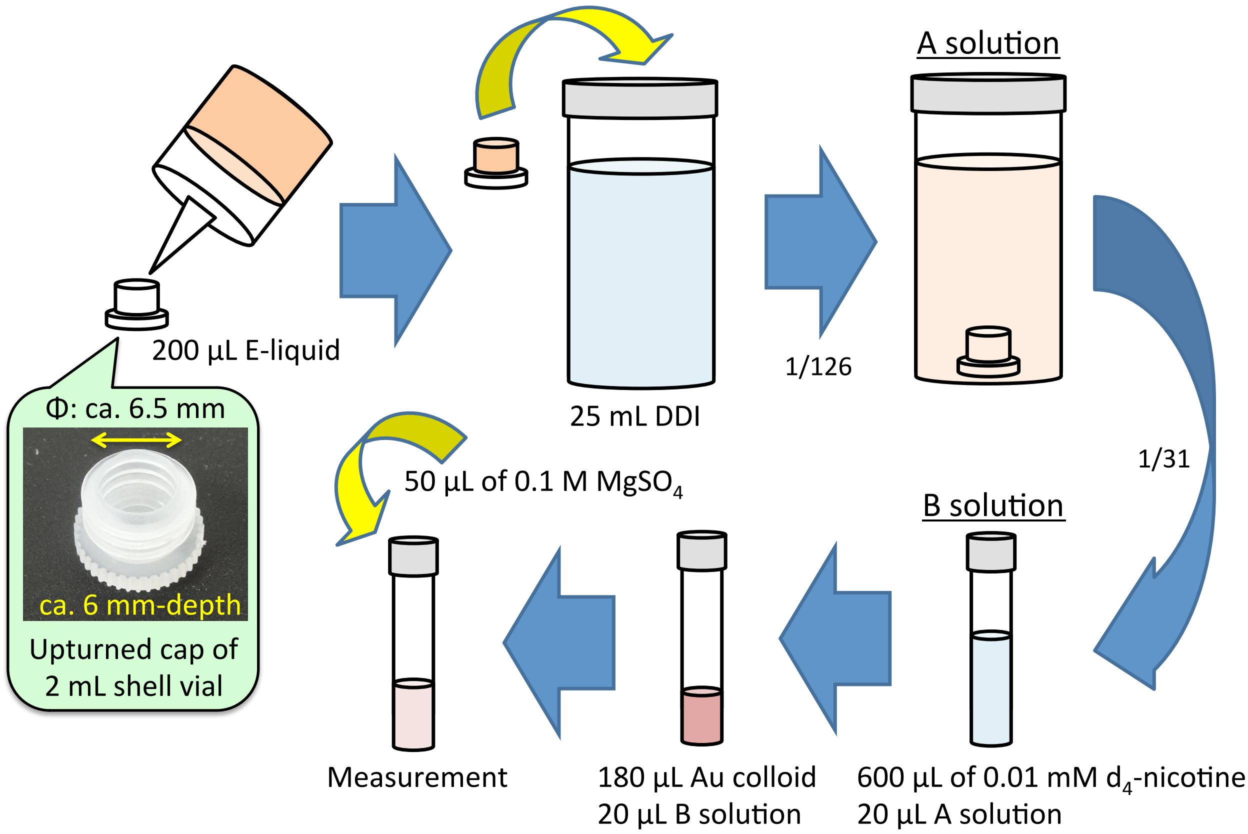

Figure S1. Scheme of sample preparation.

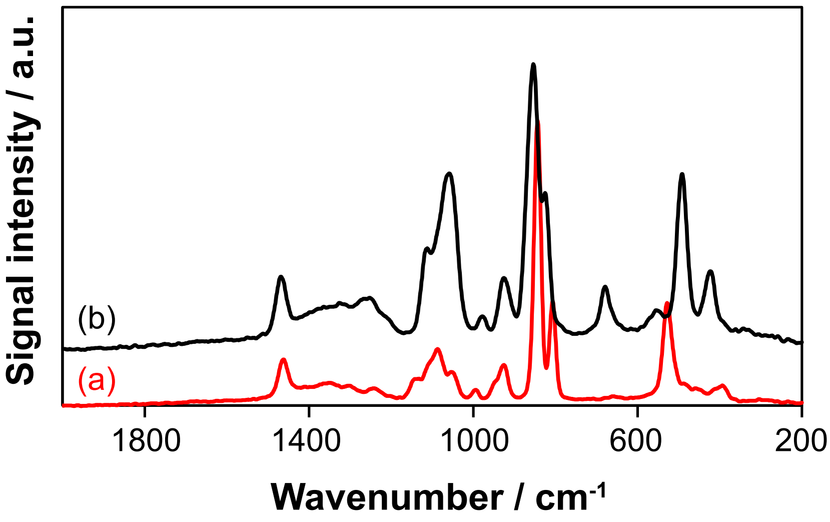

Figure S2. Raman spectra of (a) propylene glycol and (b) vegetable glycerin.

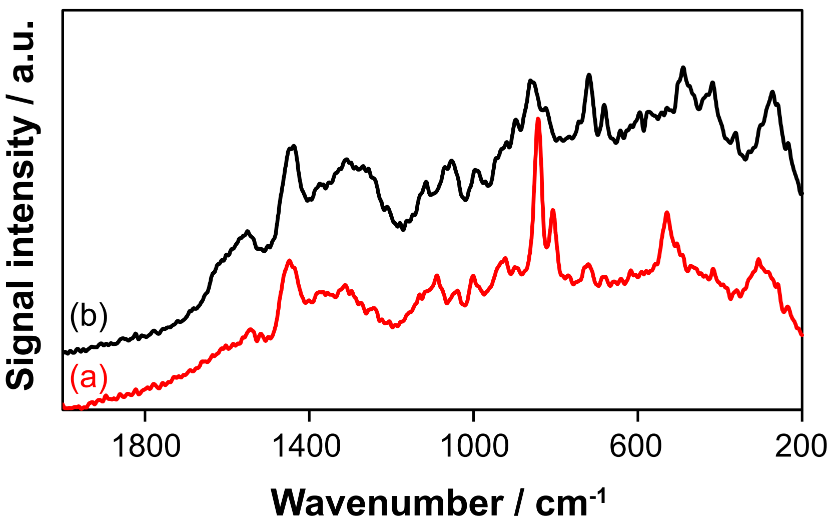

Figure S3. Spectra of (a) propylene glycol and (b) vegetable glycerine mixed with colloid and aggregating agent.

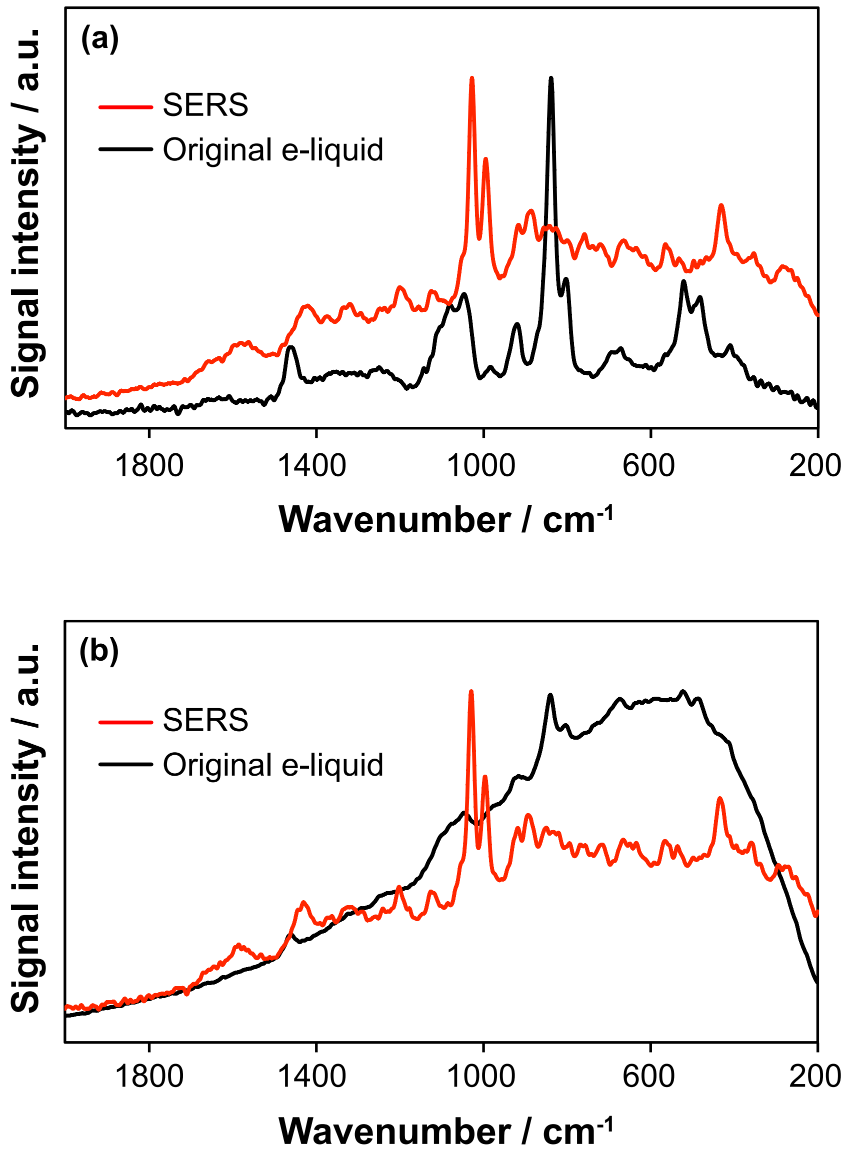

Figure S4. (a) Raman and SERS spectra of tobacco flavored e-liquid containing fresh nicotine at 18 mg mL^{-1}. (b) Raman and SERS spectra of vanilla flavored e-liquid containing old nicotine at 18 mg mL^{-1}. In both SERS spectra the samples were spiked with d_4-nicotine to give a final concentration of 10 μM.

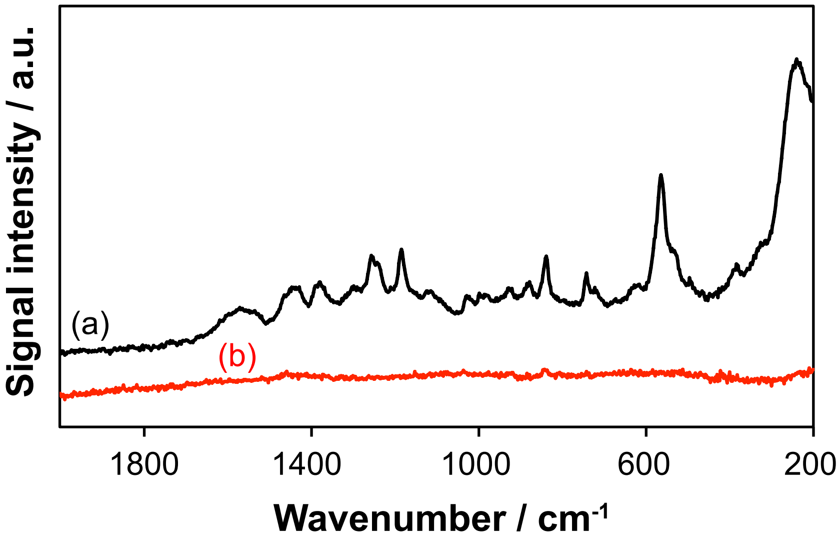

Figure S5. (a) Blank SERS spectrum of aggregated colloid showing bands of the organic stabilizing layer (b) SERS spectrum with undiluted tobacco flavoured e-liquid showing disappearance of the colloid's background signal. Samples were prepared from of 20 μL of e-liquid (or water in the blank), 180 μL of Au colloid solution and 50 μL of 0.1 M $MgSO_4$. Spectra are on the same intensity scale.

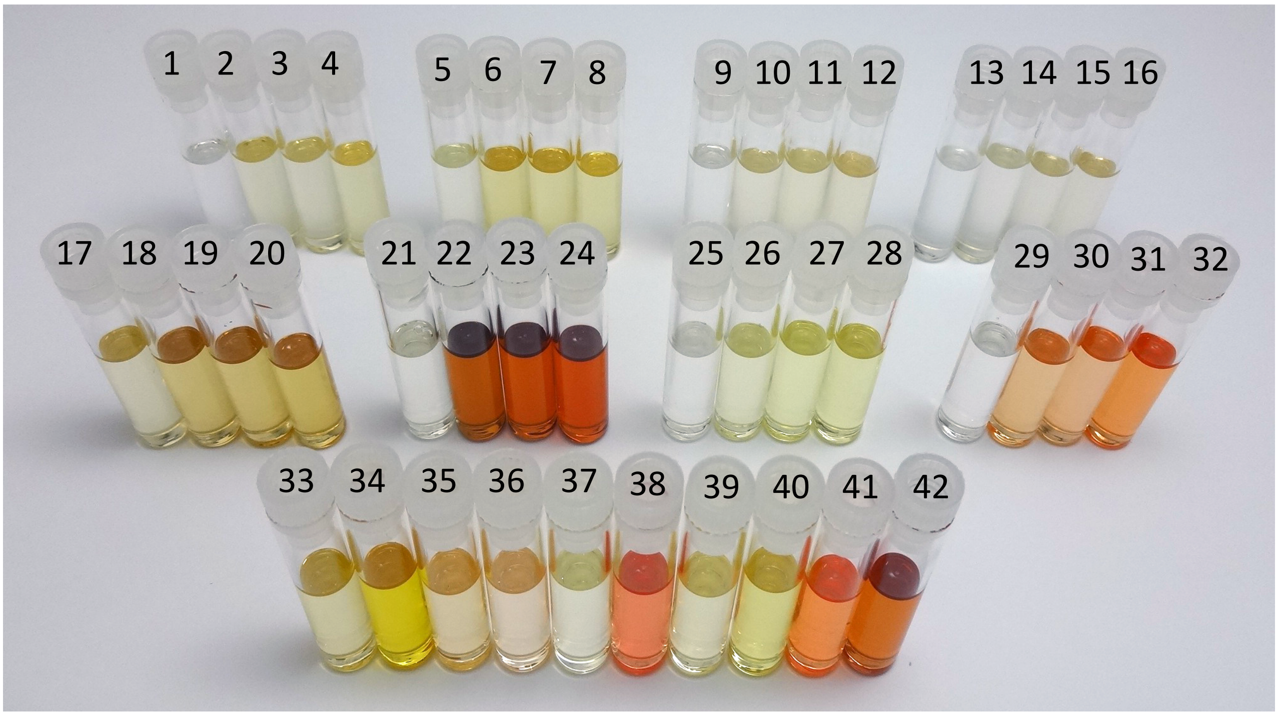

Figure S6. Photo of all e-liquids examined in this study. Numbers on vials are corresponding to those in Fig. 6 and Tables S1−S3.

Table S1. Information of e-liquids examined in this study.

Sample No.	Category	Name	Nicotine level[a]	Manufacturer	Type of base
1	Tobacco 1	RY4	0	CigElectric	PG/VG = 7/3
2		RY4	6	CigElectric	PG/VG = 7/3
3		RY4	12	CigElectric	PG/VG = 7/3
4		RY4	18	CigElectric	PG/VG = 7/3
5	Tobacco 2	Tobacco Blend	0	CigElectric	PG/VG = 7/3
6		Tobacco Blend	6	CigElectric	PG/VG = 7/3
7		Tobacco Blend	12	CigElectric	PG/VG = 7/3
8		Tobacco Blend	18	CigElectric	PG/VG = 7/3
9	Menthol 1	Menthol	0	CigElectric	PG/VG = 7/3
10		Menthol	6	CigElectric	PG/VG = 7/3
11		Menthol	12	CigElectric	PG/VG = 7/3
12		Menthol	18	CigElectric	PG/VG = 7/3
13	Menthol 2	Menthol Sensation	0	CigElectric	PG/VG = 7/3
14		Menthol Sensation	6	CigElectric	PG/VG = 7/3
15		Menthol Sensation	12	CigElectric	PG/VG = 7/3
16		Menthol Sensation	18	CigElectric	PG/VG = 7/3
17	Coffee	Coffee	0	CigElectric	PG/VG = 7/3
18		Coffee	6	CigElectric	PG/VG = 7/3
19		Coffee	12	CigElectric	PG/VG = 7/3
20		Coffee	18	CigElectric	PG/VG = 7/3
21	Vanilla	Vanilla	0	CigElectric	PG/VG = 7/3
22		Vanilla	6	CigElectric	PG/VG = 7/3
23		Vanilla	12	CigElectric	PG/VG = 7/3
24		Vanilla	18	CigElectric	PG/VG = 7/3
25	Fruit 1	Juicy Peach	0	CigElectric	PG/VG = 7/3
26		Juicy Peach	6	CigElectric	PG/VG = 7/3
27		Juicy Peach	12	CigElectric	PG/VG = 7/3
28		Juicy Peach	18	CigElectric	PG/VG = 7/3
29	Fruit 2	Fruit mix	0	CigElectric	PG/VG = 7/3
30		Fruit mix	6	CigElectric	PG/VG = 7/3
31		Fruit mix	12	CigElectric	PG/VG = 7/3
32		Fruit mix	18	CigElectric	PG/VG = 7/3

Table S1 continued

Sample No.	Category	Name	Nicotine level[a]	Manufacturer	Type of base
33	Assorted liquids	Golden Tobacco	11	Vivid Vapours	PG
34		Classic Tobacco	11	Vivid Vapours	PG
35		Menthol Breeze	11	Vivid Vapours	PG
36		Fruit Fusion	11	Vivid Vapours	PG
37		Pineapple Rocks	11	Vivid Vapours	PG
38		Berry Blast	11	Vivid Vapours	PG
39		Citrus Fruit	11	Vivid Vapours	PG
40		Apricot Peach	11	Vivid Vapours	PG
41		Cinnamon Apple	11	Vivid Vapours	PG
42		Red Wings	11	Vivid Vapours	PG

a, Values of nicotine shown on their containers

PG: mono propylene glycol, VG: vegetable glycerin

Table S2. Matching factors of each e-liquid spectrum with calibration solutions.

Sample No	Nicotine level[a] / mg	Iteration	Each matching factor with calibration level					
			0 mg	3 mg	6 mg	12 mg	18 mg	24 mg
1	0	1	0.980	0.910	0.820	0.610	0.440	0.340
		2	0.980	0.890	0.780	0.570	0.390	0.280
2	6	1	0.730	0.910	0.980	0.950	0.880	0.830
		2	0.730	0.910	0.950	0.920	0.840	0.790
3	12	1	0.550	0.800	0.920	0.980	0.970	0.940
		2	0.570	0.810	0.930	0.980	0.960	0.930
4	18	1	0.420	0.710	0.870	0.970	0.990	0.970
		2	0.370	0.670	0.850	0.960	0.990	0.980
5	0	1	0.980	0.910	0.800	0.590	0.400	0.300
		2	0.980	0.890	0.780	0.560	0.380	0.270
6	6	1	0.760	0.920	0.980	0.940	0.860	0.800
		2	0.740	0.920	0.980	0.950	0.880	0.820
7	12	1	0.570	0.810	0.930	0.980	0.960	0.920
		2	0.570	0.820	0.930	0.980	0.950	0.920
8	18	1	0.370	0.670	0.840	0.960	0.990	0.980
		2	0.400	0.700	0.860	0.960	0.980	0.970
9	0	1	0.980	0.900	0.800	0.590	0.410	0.300
		2	0.980	0.900	0.790	0.580	0.400	0.290
10	6	1	0.760	0.930	0.980	0.940	0.860	0.800
		2	0.780	0.920	0.980	0.930	0.850	0.780
11	12	1	0.560	0.800	0.930	0.980	0.960	0.930
		2	0.570	0.820	0.930	0.980	0.950	0.920
12	18	1	0.380	0.690	0.850	0.960	0.990	0.980
		2	0.390	0.690	0.850	0.960	0.990	0.980
13	0	1	0.980	0.900	0.790	0.570	0.390	0.280
		2	0.980	0.900	0.800	0.590	0.420	0.310
14	6	1	0.780	0.940	0.970	0.920	0.830	0.770
		2	0.820	0.940	0.970	0.900	0.810	0.740
15	12	1	0.610	0.840	0.950	0.980	0.940	0.910
		2	0.500	0.780	0.900	0.970	0.950	0.930
16	18	1	0.340	0.670	0.820	0.940	0.970	0.970
		2	0.390	0.690	0.860	0.960	0.990	0.980

Table S2 continued

Sample No	Nicotine level[a] / mg	Iteration	Each matching factor with calibration level					
			0 mg	3 mg	6 mg	12 mg	18 mg	24 mg
17	0	1	0.980	0.900	0.790	0.570	0.390	0.280
		2	0.980	0.910	0.800	0.590	0.410	0.300
18	6	1	0.770	0.930	0.980	0.930	0.850	0.790
		2	0.750	0.930	0.980	0.950	0.870	0.810
19	12	1	0.610	0.840	0.950	0.980	0.950	0.910
		2	0.550	0.810	0.920	0.980	0.960	0.920
20	18	1	0.370	0.670	0.840	0.960	0.990	0.980
		2	0.370	0.680	0.840	0.950	0.980	0.970
21	0	1	0.970	0.900	0.780	0.570	0.380	0.280
		2	0.980	0.910	0.790	0.580	0.400	0.290
22	6	1	0.750	0.920	0.970	0.940	0.850	0.800
		2	0.760	0.920	0.960	0.920	0.830	0.770
23	12	1	0.490	0.770	0.900	0.980	0.970	0.950
		2	0.560	0.810	0.930	0.980	0.960	0.930
24	18	1	0.390	0.690	0.860	0.960	0.980	0.970
		2	0.380	0.680	0.840	0.960	0.980	0.980
25	0	1	0.990	0.900	0.790	0.570	0.390	0.280
		2	0.980	0.890	0.780	0.560	0.380	0.270
26	6	1	0.780	0.930	0.980	0.920	0.840	0.770
		2	0.770	0.920	0.980	0.930	0.850	0.790
27	12	1	0.500	0.770	0.910	0.980	0.970	0.950
		2	0.520	0.780	0.910	0.980	0.970	0.950
28	18	1	0.390	0.680	0.850	0.970	0.990	0.980
		2	0.390	0.690	0.860	0.970	0.990	0.980
29	0	1	0.930	0.890	0.760	0.560	0.380	0.290
		2	0.980	0.910	0.790	0.580	0.390	0.290
30	6	1	0.730	0.910	0.970	0.950	0.870	0.810
		2	0.760	0.920	0.970	0.940	0.860	0.790
31	12	1	0.570	0.820	0.930	0.980	0.960	0.930
		2	0.530	0.790	0.920	0.980	0.970	0.940
32	18	1	0.400	0.690	0.860	0.960	0.980	0.970
		2	0.390	0.690	0.850	0.960	0.980	0.970

Table S2 continued

Sample No	Nicotine level[a] / mg	Iteration	Each matching factor with calibration level					
			0 mg	3 mg	6 mg	12 mg	18 mg	24 mg
33	11	1	0.580	0.820	0.940	<u>0.980</u>	0.950	0.920
		2	0.570	0.820	0.940	<u>0.980</u>	0.950	0.920
34	11	1	0.570	0.820	0.930	<u>0.980</u>	0.960	0.930
		2	0.610	0.830	0.940	<u>0.980</u>	0.950	0.910
35	11	1	0.540	0.800	0.920	<u>0.980</u>	0.970	0.940
		2	0.600	0.830	0.950	<u>0.980</u>	0.950	0.910
36	11	1	0.570	0.810	0.930	<u>0.980</u>	0.960	0.930
		2	0.600	0.830	0.950	<u>0.980</u>	0.950	0.920
37	11	1	0.630	0.860	0.950	<u>0.980</u>	0.940	0.900
		2	0.620	0.850	0.950	<u>0.980</u>	0.940	0.900
38	11	1	0.590	0.830	0.940	<u>0.980</u>	0.960	0.920
		2	0.550	0.810	0.930	<u>0.980</u>	0.960	0.930
39	11	1	0.540	0.800	0.920	<u>0.980</u>	0.970	0.940
		2	0.560	0.820	0.930	<u>0.980</u>	0.960	0.930
40	11	1	0.650	0.860	0.960	<u>0.970</u>	0.930	0.880
		2	0.580	0.820	0.930	<u>0.980</u>	0.950	0.920
41	11	1	0.690	0.870	<u>0.960</u>	<u>0.960</u>	0.910	0.850
		2	0.640	0.860	0.950	<u>0.960</u>	0.920	0.880
42	11	1	0.680	0.870	<u>0.970</u>	0.960	0.920	0.860
		2	0.670	0.870	<u>0.960</u>	<u>0.960</u>	0.910	0.870

Underlined values are highest matching factor among nicotine levels examined.

a, Nicotine level shown on each e-liquid container.