Coupled Electrochemical Mass Spectrometry Investigations of the Oxidation of Nicotine and Its Determination in Third-Hand Smoke by Liquid Chromatography Electrochemical Detection

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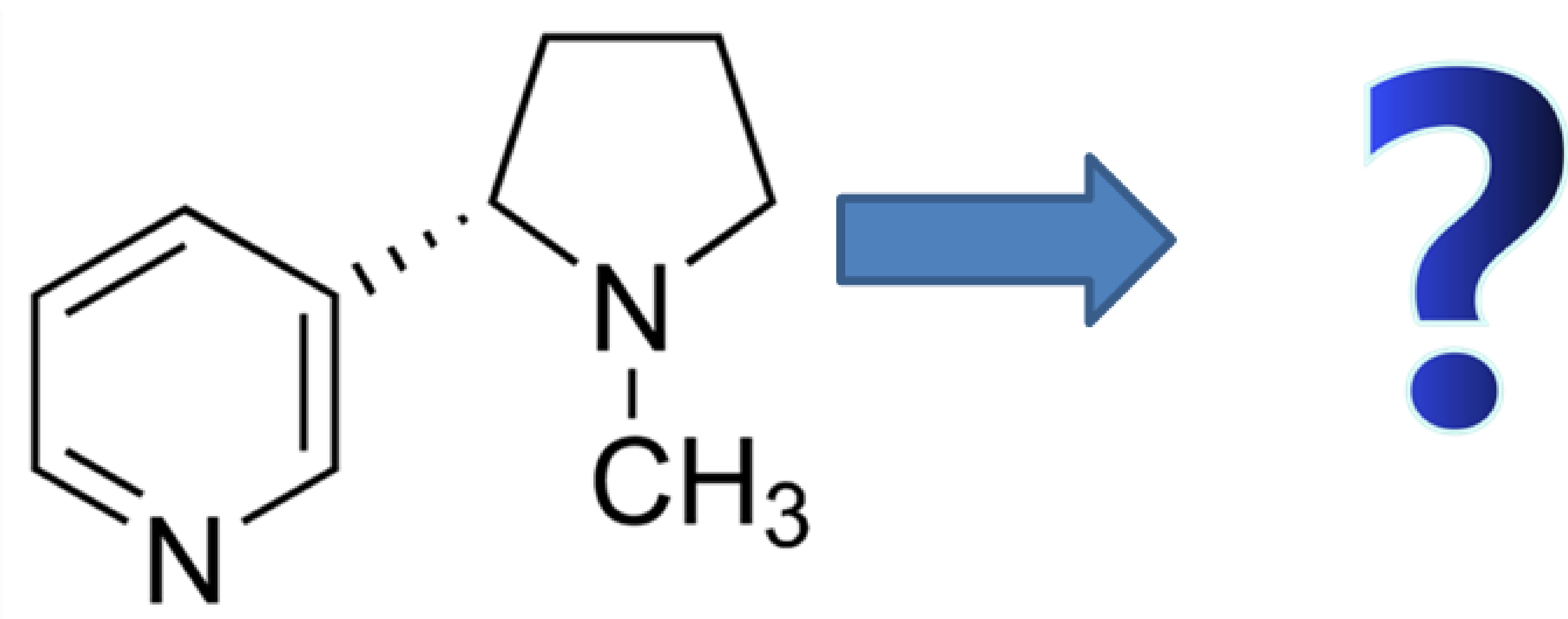
Outline of Talk

- The electrochemistry of nicotine
- Electrochemical mass spectrometry of nicotine
- What is third-hand smoke?
- Why is it important environmentally?
- Liquid chromatography electrochemical detection of third-hand smoke
- Conclusions

Electrochemistry of Nicotine

The tobacco plant is native to the Americas and its use as a medicine and stimulant goes back at least 2000 years and most likely many millennia before that.

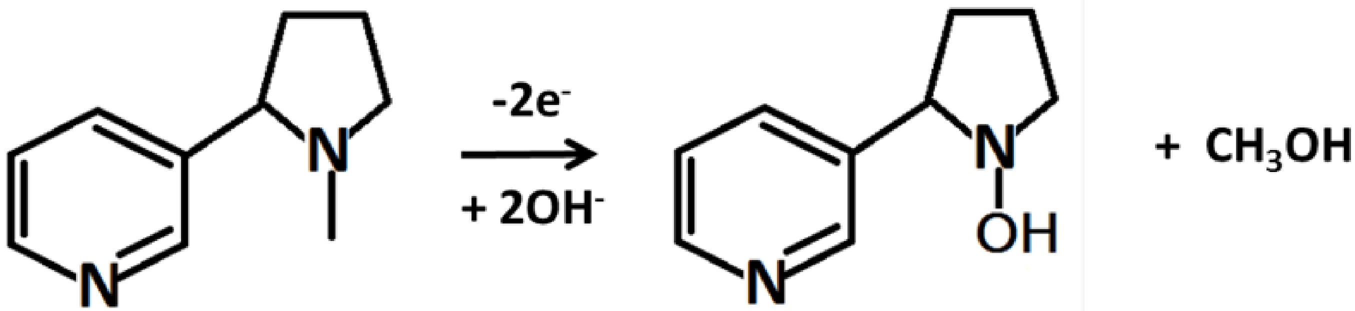
Cigarettes were invented in 1614 by beggars in Seville, who collected scraps of cigars and rolled the tobacco into small pieces of paper.



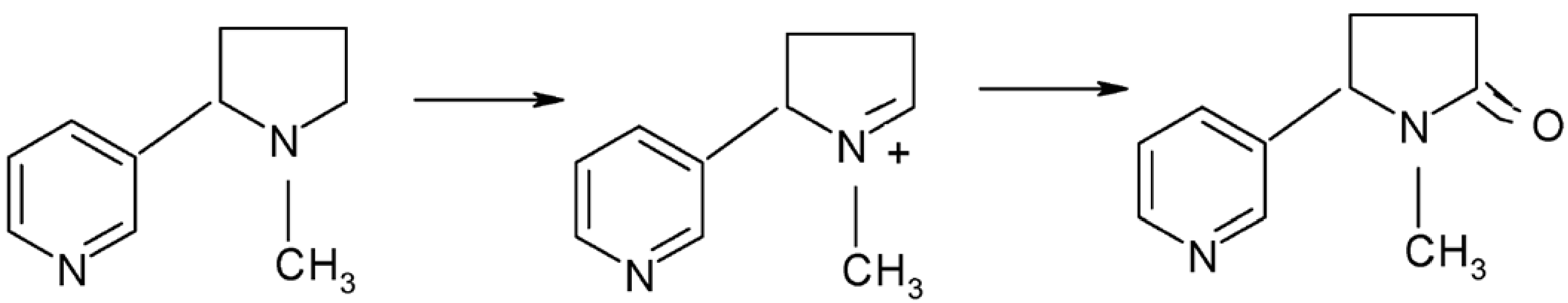
Electrochemistry of Nicotine

The majority of reports show nicotine to be oxidised in a single oxidation process at high pH values.

High hydroxyl ion concentration aids in the demethylation and subsequent hydroxylation of the nitrogen of the pyrrolidine ring.

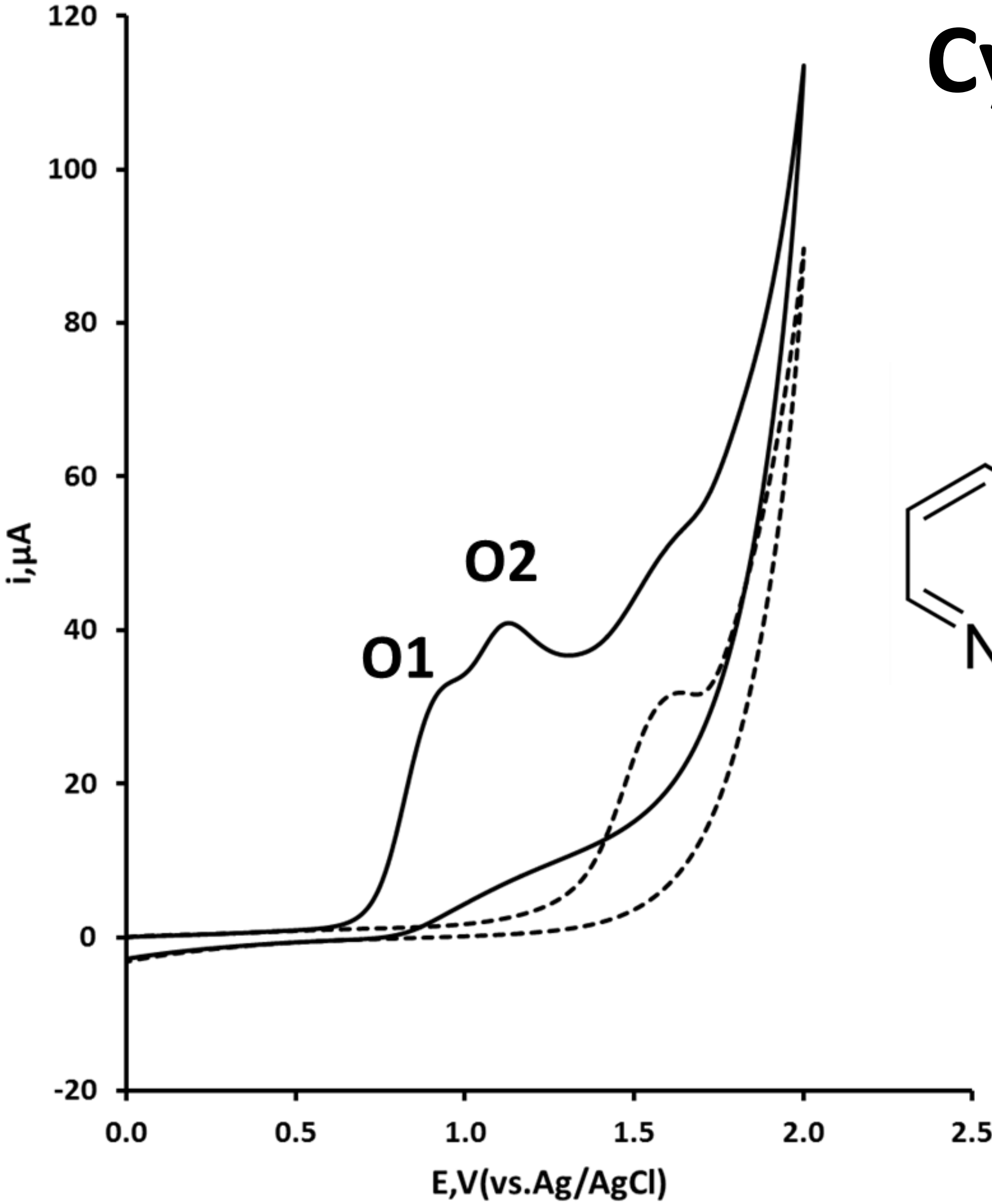


Or the 2e oxidation of nicotine in the presence of water to form cotinine, its biological metabolite.



Nicotine nicotina-Δ-1'(5') iminiun ion Cotinine

Cyclic Voltammetry of Nicotine



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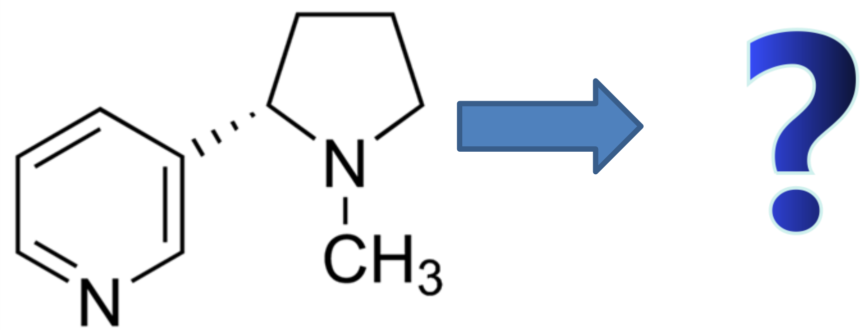
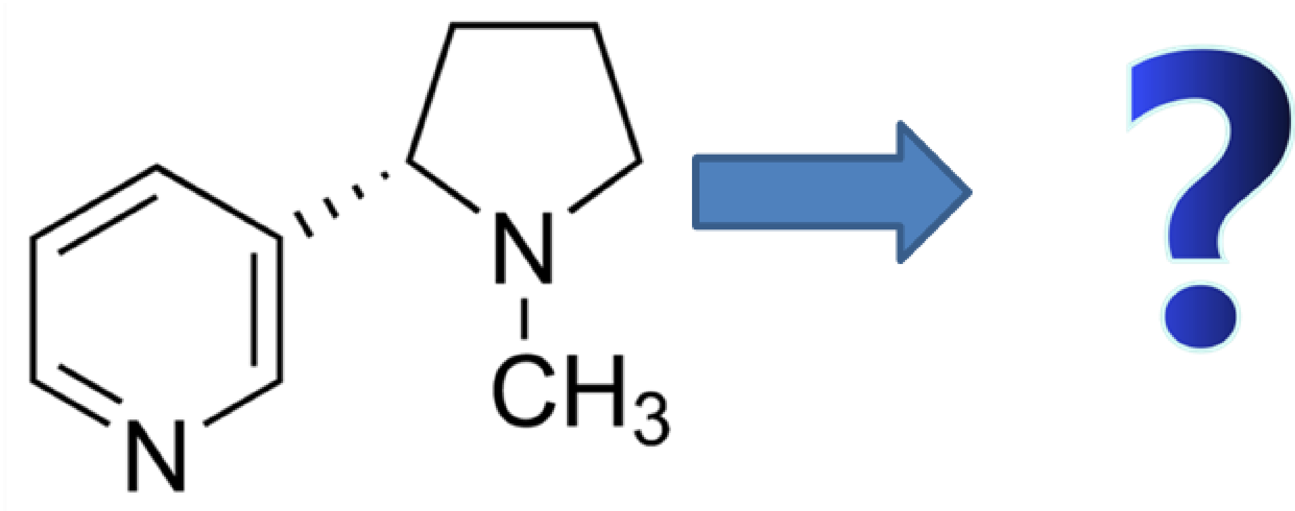


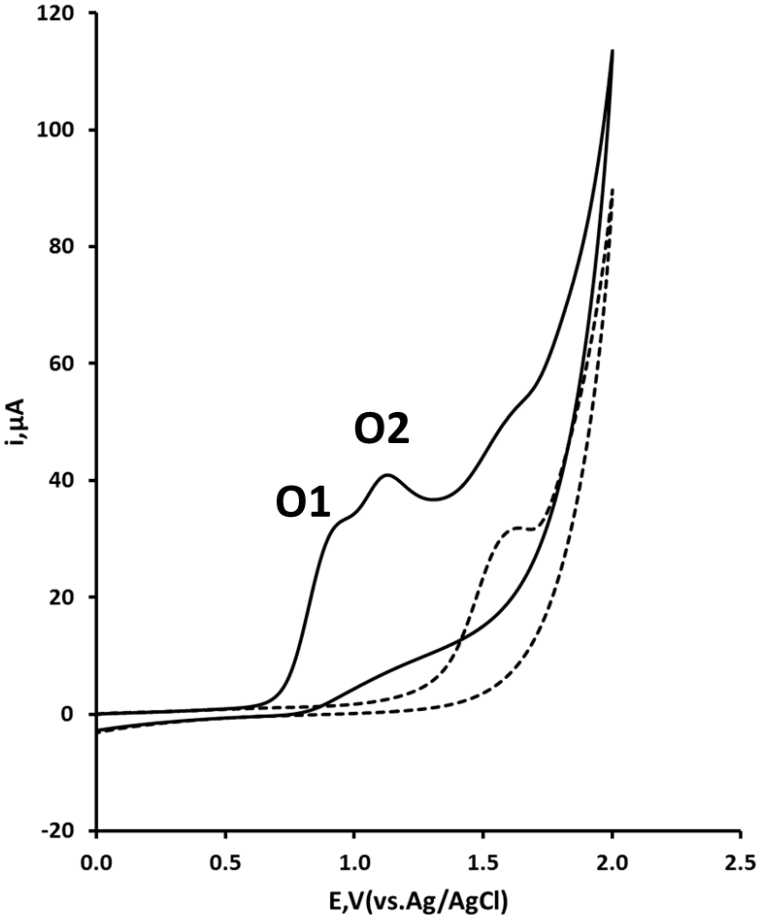
Figure 1. Typical cyclic voltammogram, obtained at a scan rate of 50 mV/s, for dashed line, in the absence of and solid line in the presence of 2 mM nicotine in 10 % acetonitrile, buffered with 0.1 M phosphate at pH 10. Starting potential 0.0 V; switching potential +2.0 V.

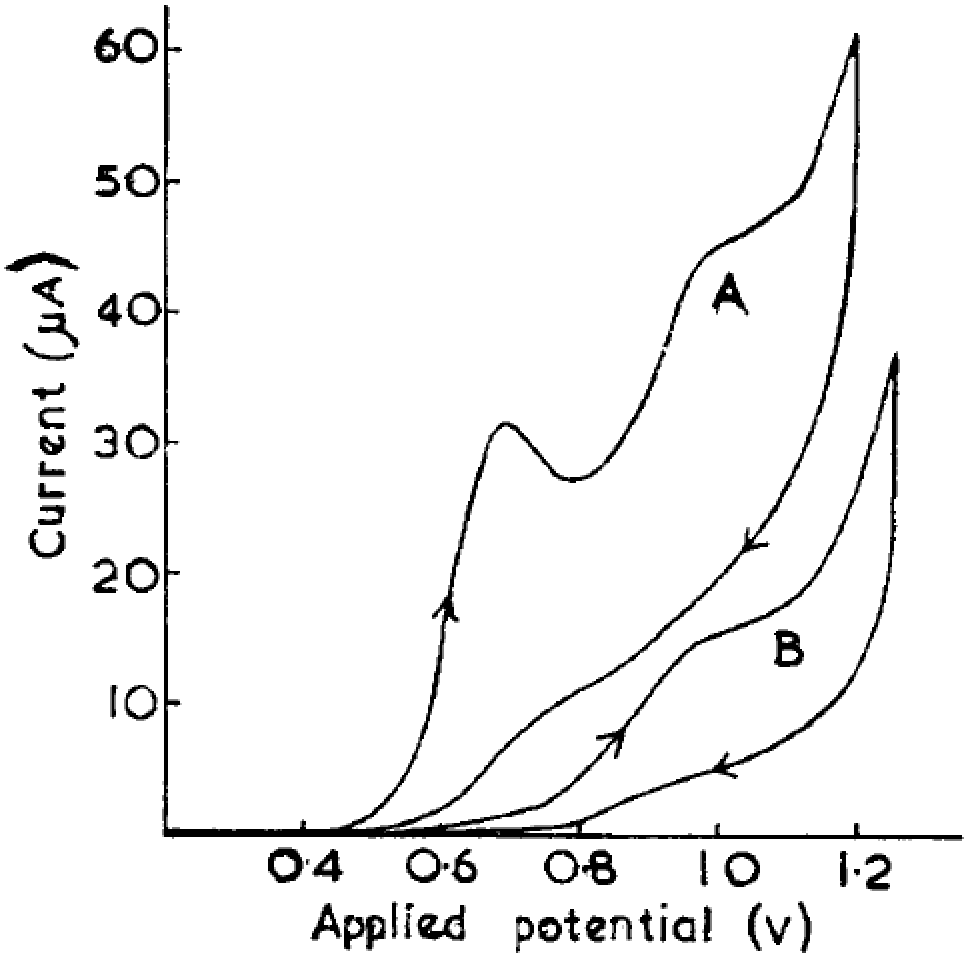


My Hypothesis

Anodic Oxidation of Amines. Part I. Cyclic Voltammetry of Aliphatic Amines at a Stationary Glassy-carbon Electrode

By Masaichiro Masui,* Hiroteru Sayo, and Yoshiaki Tsuda, Faculty of Pharmaceutical Sciences, Osaka





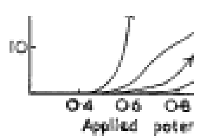


FIGURE 1 Cyclic voltammograms of (A) triethylamine a (B) diethylamine; pH 11·9, 2 mM, 37 mv sec.[-1]

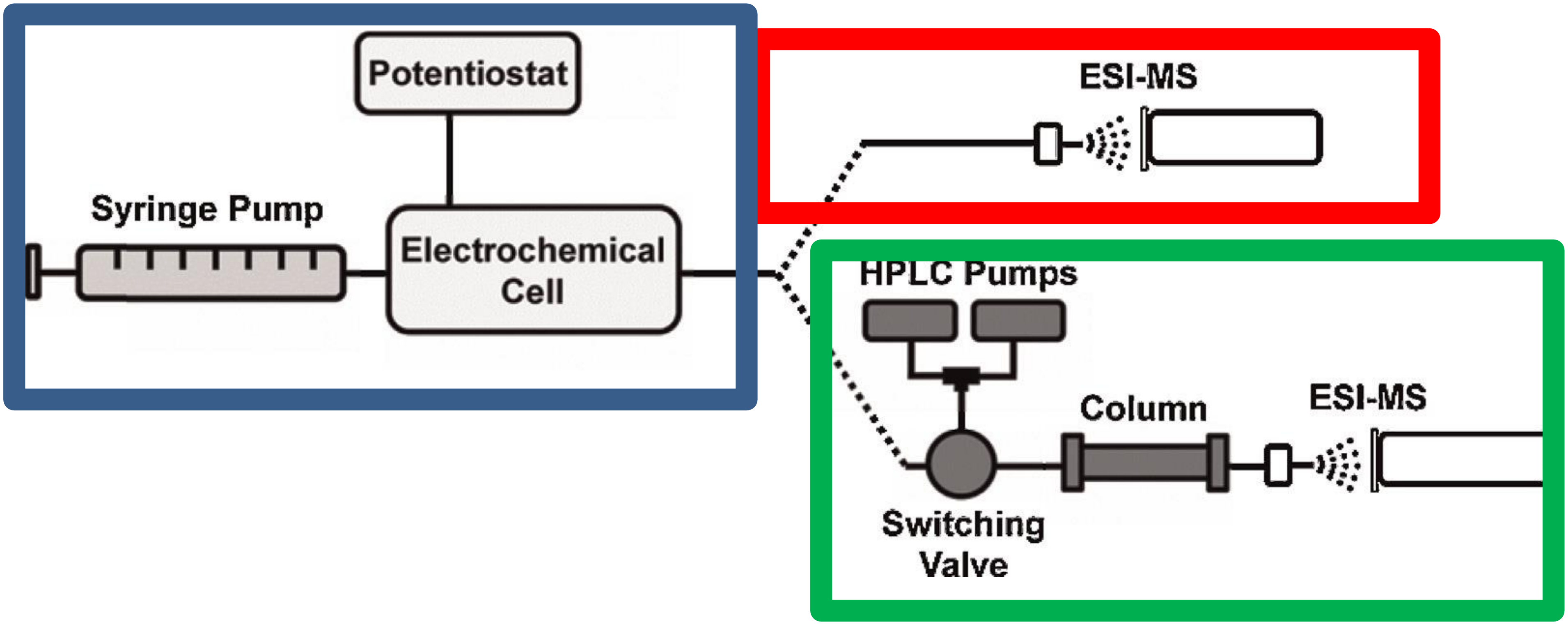
FIGURE 1 Cyclic voltammograms o (B) diethylamine; pH 11·9, 2

of the second wave closely resembled that of diethylamine at the same pH value. The peak current (i_p) of the first

of the scan rate was obtained over scan rates ranging from 9 to 231 mv sec.[-1] (Figure 4). There was no sign of a

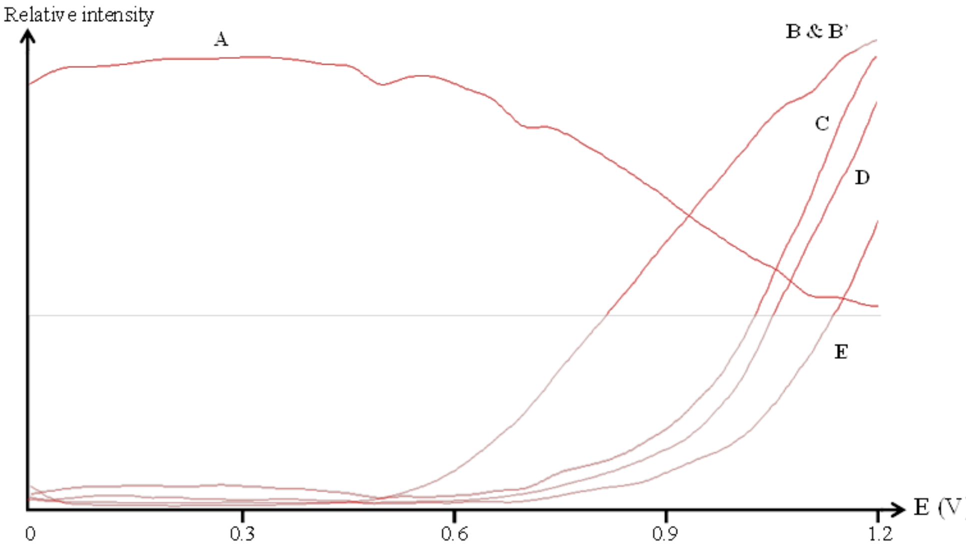
[4] R. F. Dano and C. K. Mann, *Analyt. Chem.*, 1963, **35**, 677.

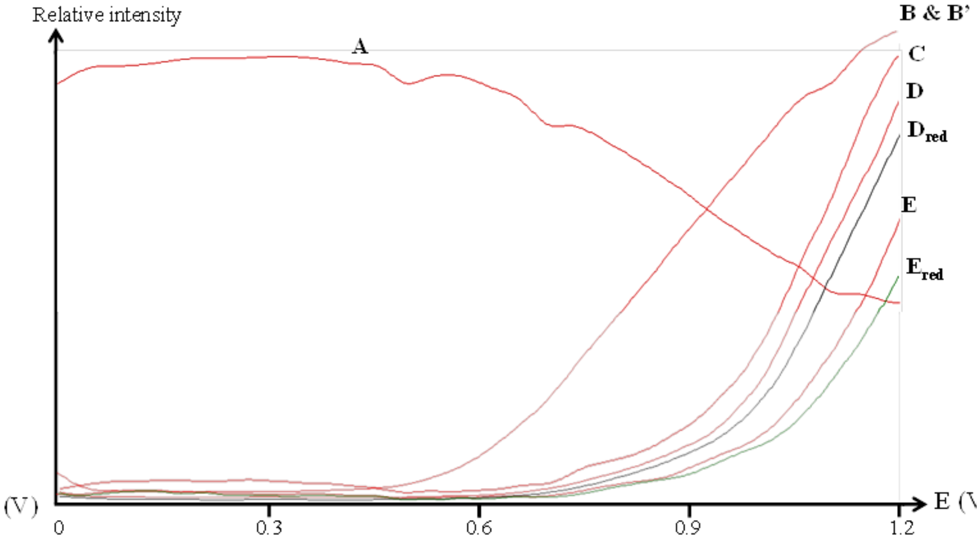
Electrochemical Mass Spectrometry

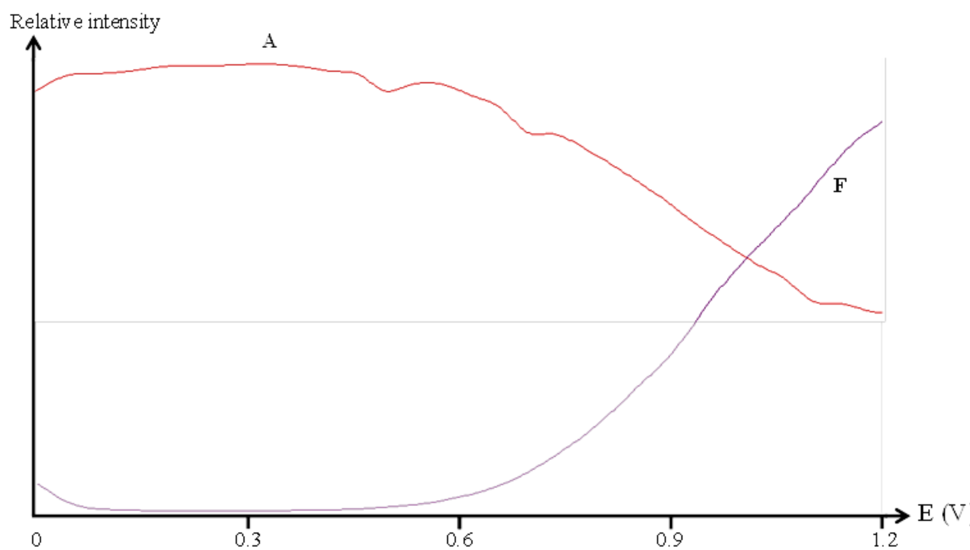


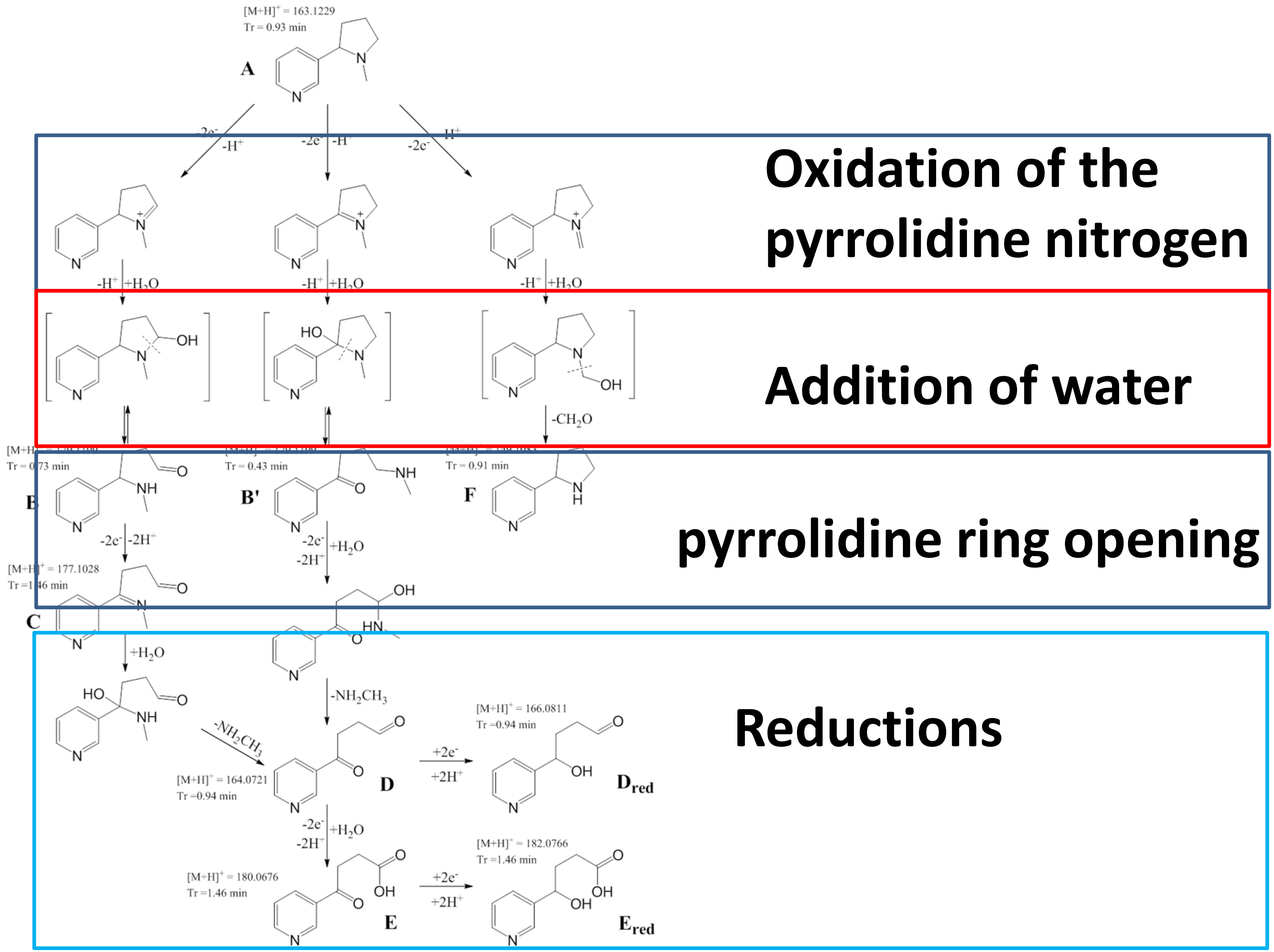
General set-ups used for EC/LC/MS: Mass voltammograms are recorded after direct connection of the EC cell effluent to the MS (upper route). The lower route is used to separate electrogenerated products prior to MS by collection of the EC cell effluent in an injection valve and subsequent injection of the analyte filled in the loop.

H. Faber, M. Vogel, U. Karst , *Anal. Chim. Acta* 834 (2014) 9–21 .


Relative intensity
A
B & B'
C
D
E
0
0.3
0.6
0.9
1.2
E (V)


Relative intensity
A
B & B'
C
D
D_{red}
E
E_{red}
0
0.3
0.6
0.9
1.2


Relative intensity
A
F
0
0.3
0.6
0.9
1.2
E (V)



Oxidation of the pyrrolidine nitrogen
Addition of water
pyrrolidine ring opening
Reductions
[M+H]+ = 163.1229
Tr = 0.93 min
A
-2e-
-H+
-2e- -H+
H+
-2e-
-H+ +H2O
-H+ +H2O
-H+ +H2O
-CH2O
Tr = 0.43 min
Tr = 0.91 min
B'
F
B
-2e- -2H+
-2e-
+H2O
-2H+
[M+H]+ = 177.1028
C
+H2O
-NH2CH3
-NH2CH3
[M+H]+ = 164.0721
Tr =0.94 min
D
+2e-
+2H+
[M+H]+ = 166.0811
Tr =0.94 min
Dred
-2e-
-2H+
+H2O
[M+H]+ = 180.0676
Tr =1.46 min
E
+2e-
+2H+
[M+H]+ = 182.0766
Tr =1.46 min
Ered

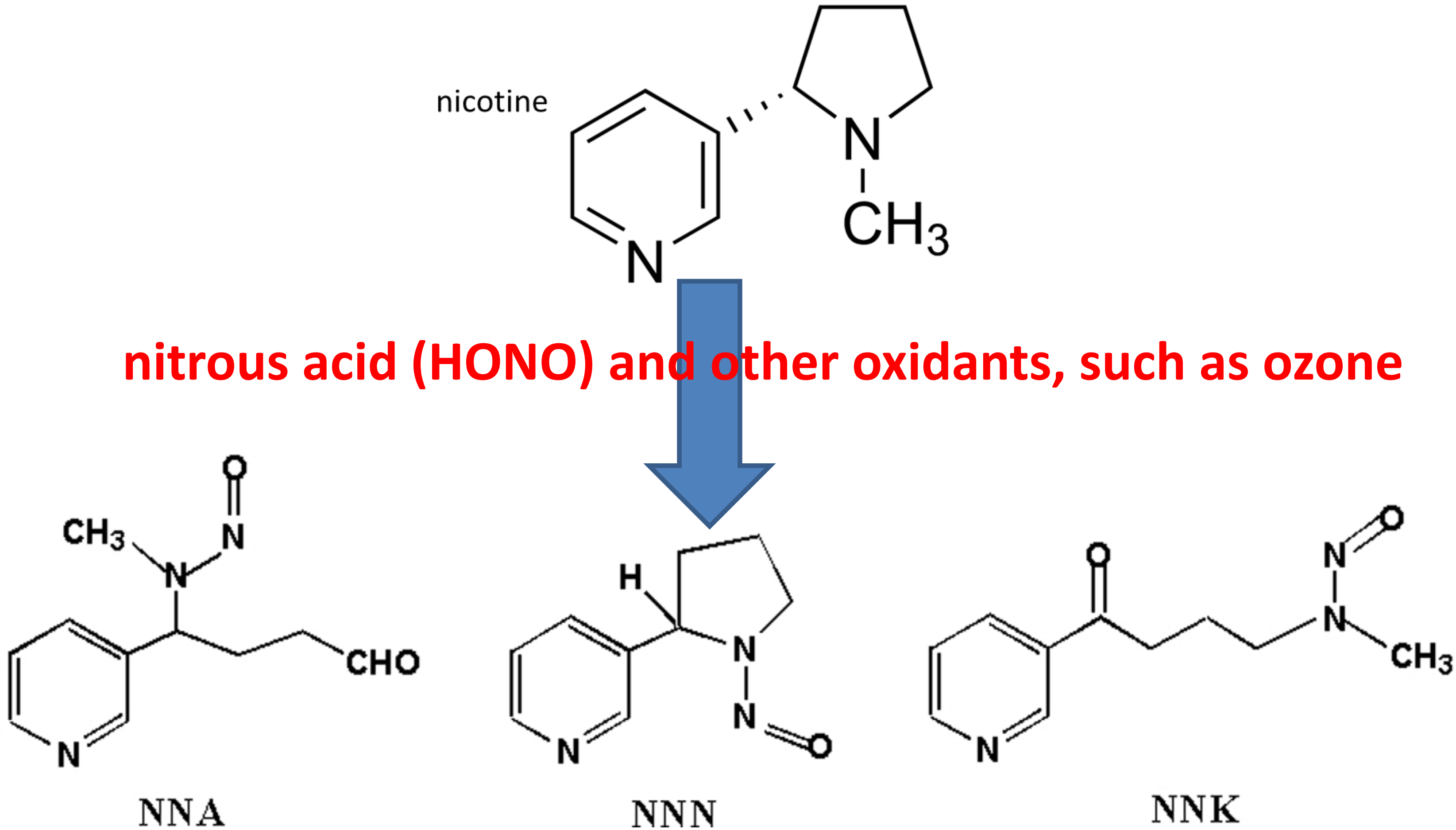
Liquid Chromatographic Electrochemical Detection of Nicotine in Third Hand Smoke

First-hand smoke is defined as what is inhaled into the lungs of the smoker

Second-hand smoke is a mixture of exhaled smoke and other substances leaving the smouldering end of the cigarette that enters the atmosphere and can be inhaled by others.

Third-hand smoke (THS) is defined as the contamination that remains on the surfaces after smoking source has been removed.

Nicotine present in the tobacco smoke residue can combine with other compounds such as ozone and nitrous oxide to produce recognized carcinogens such as nitrosamines



Tobacco-specific nitrosamines (TSNAs)

B. Hang, A.H. Sarker, C. Havel, S. Saha, T.K. Hazra, S. Schick, P. Jacob III, V.K. Rehan, A. Chenna, D. Sharan, M. Sleiman, H. Destaillats, L.A. Gundel, Thirdhand smoke causes DNA damage in human cells, *Mutagenesis* 2013, 28, 381–391.

G.E. Matt, P.J.E. Quintana, H. Destaillats, L.A. Gundel, M. Sleiman, B.C. Singer, P. Jacob III, N. Benowitz, J.P. Winickoff, V. Rehan, P. Talbot, S. Schick, J. Samet, Y. Wang, B. Hang, M. Martins-Green, J.F. Pankow, M.F. Hovell, Thirdhand Tobacco Smoke: Emerging Evidence and Arguments for a Multidisciplinary Research Agenda, *Environ. Health Perspect.* 2011, 119, 1218.

Effect of pH on Nicotine Peak height

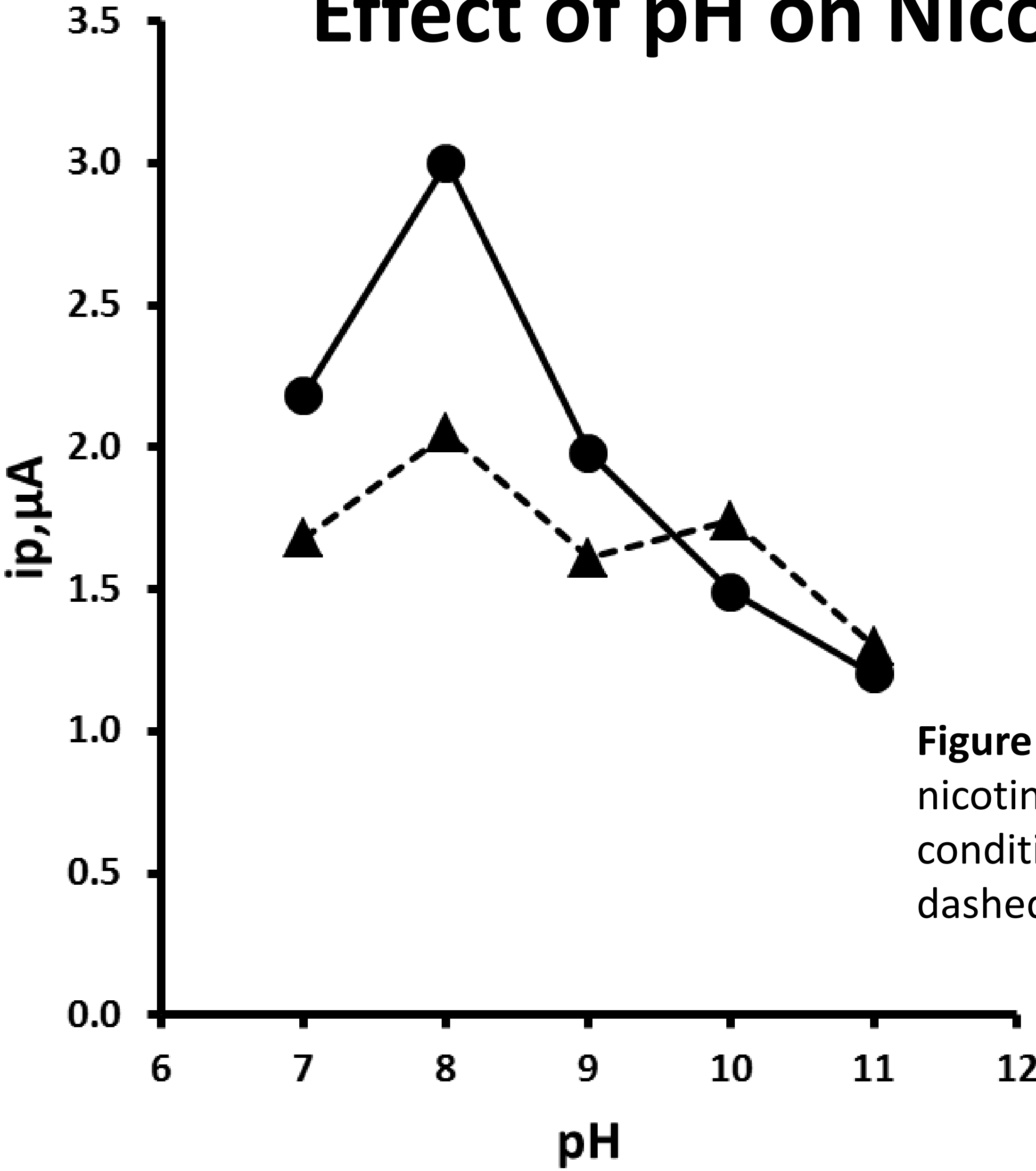


Figure 2. Plot of (a) ip vs. pH for the two nicotine oxidation peaks. Voltammetric conditions as Figure 1. O1 solid line, O2 dashed line.

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Hydrodynamic voltammogram

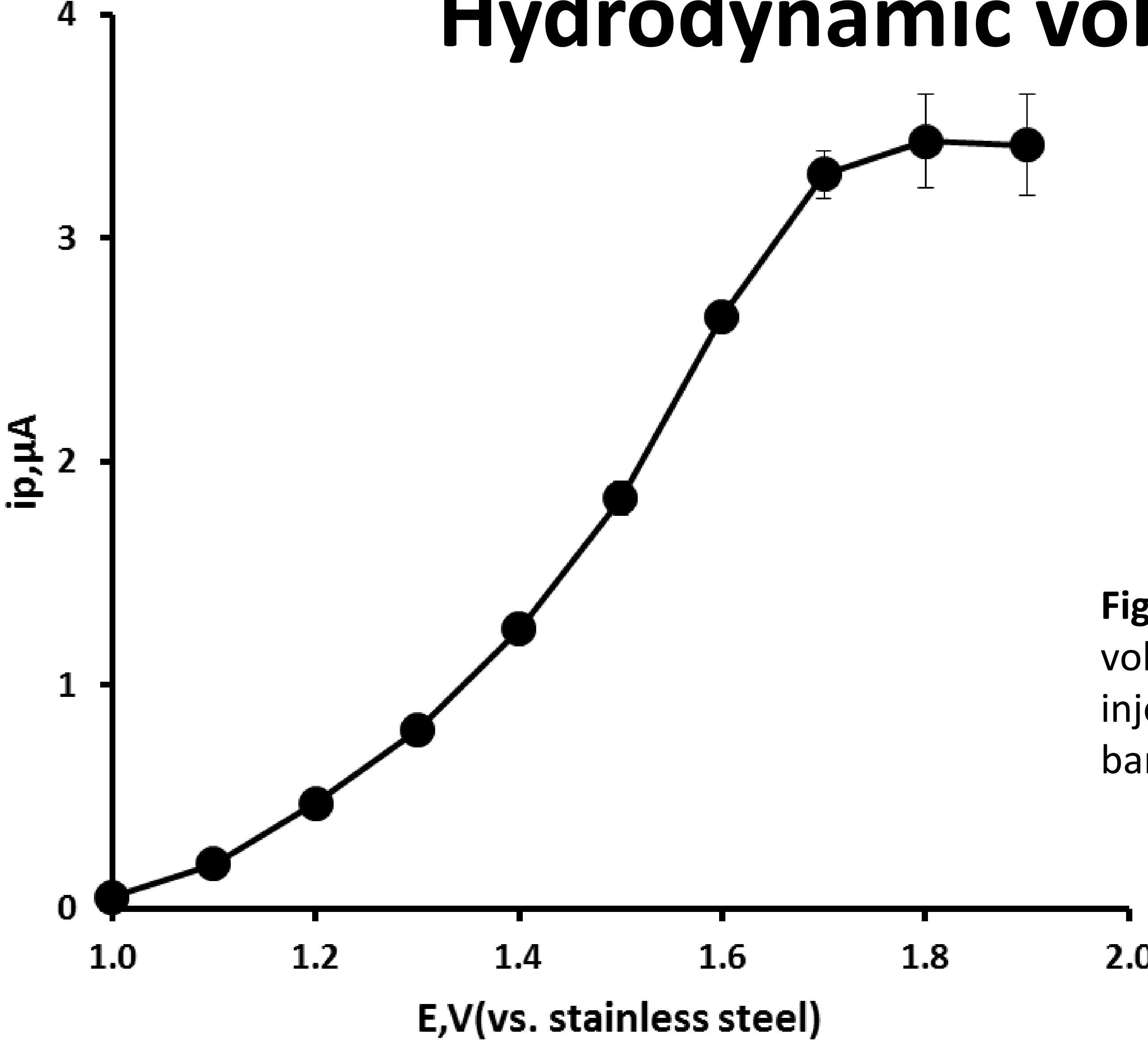

Figure 3. Hydrodynamic voltammogram for 2.6 µg injections of nicotine. Error bars represent ± σ.

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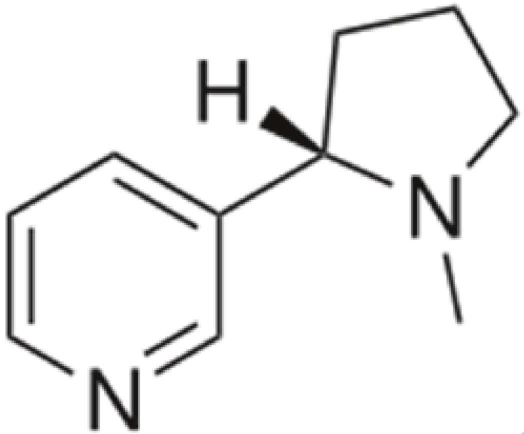
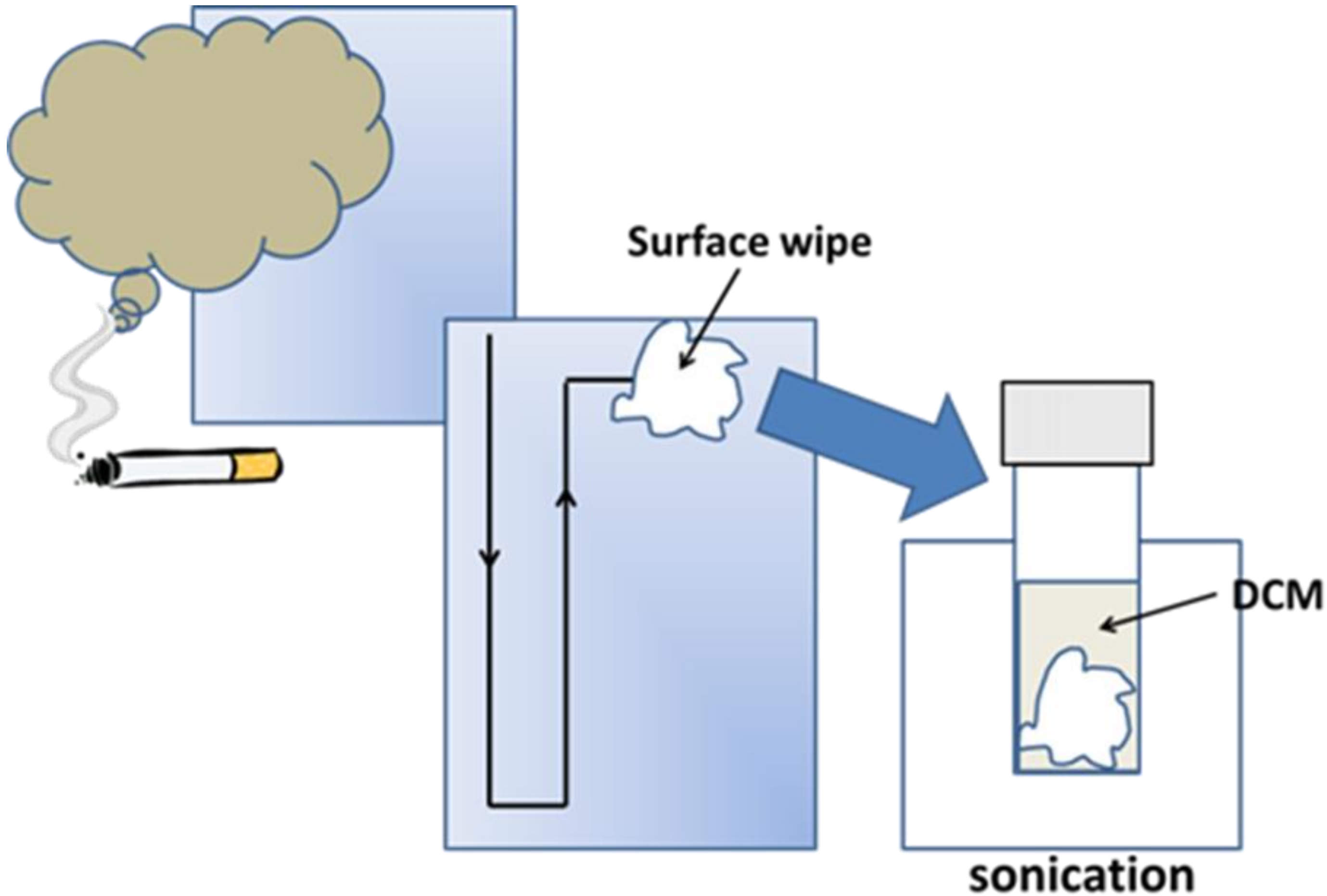


Nicotine in Third-Hand Smoke



Representative chromatograms obtained for THS dust-wipe samples.

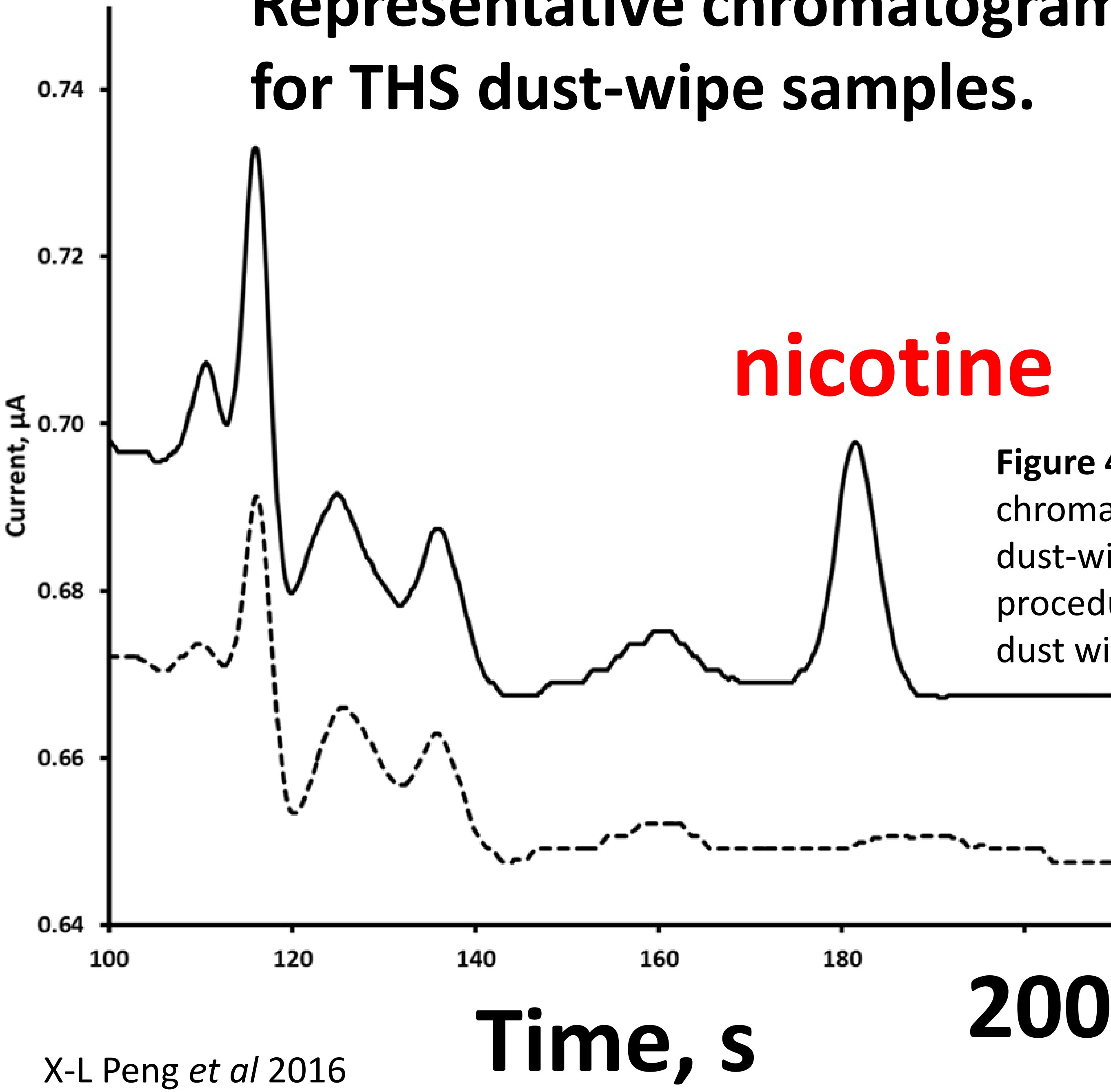


Figure 4. Representative chromatograms obtained for THS dust-wipe samples. Dashed line procedural blank, solid line THS dust wipe sample.

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Sample	Nicotine, μg/m²
1	110
2	150
3	ND
4	66.8
5	156

Table 2. Nicotine levels obtained for dust-wipe samples. ND = not detected.

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Conclusions

- Possible new explanation of the electrochemical oxidation of nicotine
- First example of the determination of nicotine as a marker of third hand smoke using liquid chromatography electrochemical detection

Acknowledgements

- Faculty of Applied Sciences for WLBs to undertake this work

Thank You for Your Attention

Peng, X.-L., Giltrow, D., Bowdler, P. and Honeychurch, K. C. (2016) Liquid chromatography electrochemical determination of nicotine in third-hand smoke, *Electroanalysis*. In press Available from: http://eprints.uwe.ac.uk/29383

Silva, S. Inácia S. e., Bowdler, P., Giltrow, D., Riddell, S. and Honeychurch, K. C. (2016) A simple and rapid method for the determination of nicotine in third-hand smoke by liquid chromatography and its application for the assessment of contaminated outdoor communal areas. *Drug Testing and Analysis,* 8 (7). pp. 676-681. Available from: http://eprints.uwe.ac.uk/25734