Development and Characterization of Microfabricated Disposable Platinum Electrodes for High Performance Ion Chromatography

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INTRODUCTION

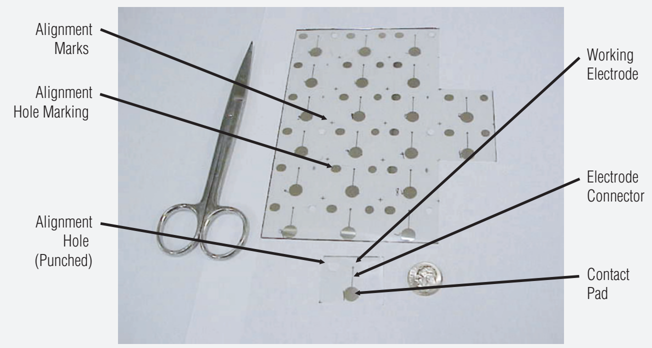
Pt Working Electrodes: Background Information

- Detection of a broad range of electro active groups
  - Hydroxy, methoxy, or amine groups in aliphatic, aromatic, and carbohydrate compounds (such as alcohols, antibiotics, phenolic antioxidants, catechols, and carbohydrates)
  - Amino thiols and other S-containing species
  - Formic acid and –OH containing organic acids
  - Inorganic Anions (such as SO_3^{2-}, S^{2-}, N_3^- and CN^-).
- Knitted PTFE reaction coil is used between the chromatographic column and the detection cell.
- Current methods with conventional Pt electrodes are not as popular as methods with Au electrodes
  - Poor reproducibility of published methods
  - Relatively difficult to develop a suitable waveform for achieving a stable detection response over a long period of time.

Why Disposable Pt Working Electrodes?

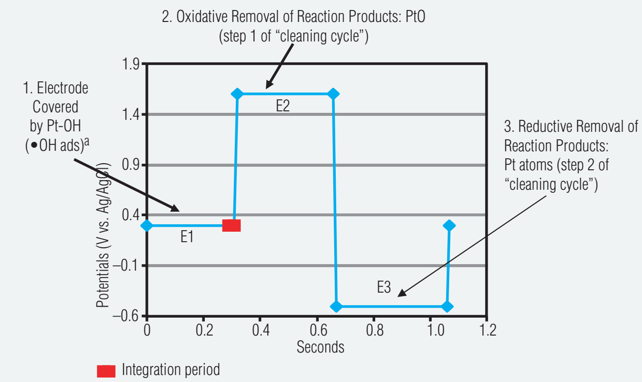
- Predictable stability of response
- Easy installation
  - Fast equilibration (minimal delay after installation)
  - Excellent electrode-to-electrode reproducibility
- No conditioning required
  - No hand polishing
  - No activation waveforms

Figure 1. Disposable Pt Working Electrodes on a Polymeric Substrate



PULSED AMPEROMETRY WAVEFORM

Figure 2. Typical Waveform for Platinum Electrodes



[a] G. Kokkinidis and D. Jannakoudakis, *J. Electroanal. Chem.* **1983,** *153,* 185.

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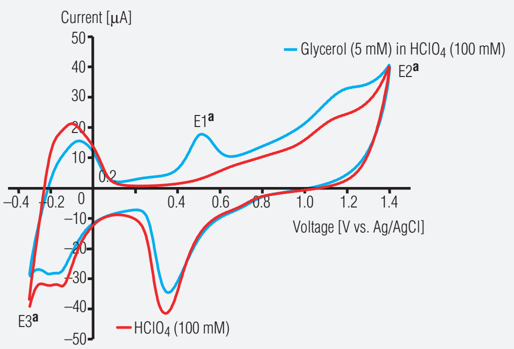
PITTCON 2006 Presentation

NEW WAVEFORM DEVELOPMENT FOR DISPOSABLE PT ELECTRODES

Cyclic Voltammetry with Disposable Platinum Electrodes

Figure 3. Cyclic Voltammetry of Glycerol Performed Inside a Chromatographic Detection Cell of a Dionex ICS-3000

Scan Rate: 28.3 mV/s



References:
1. S. Hughes, P. L. Meschi and D. C. Johnson. *Anal. Chim. Acta,* **1981,** *132,* 1.
2. W. R. LaCourse, D. C. Johnson, M. A. Rey and R. W. Slingsby, *Anal. Chem.,* **1991,** *63,* 134.

[a] Starting points for waveform development

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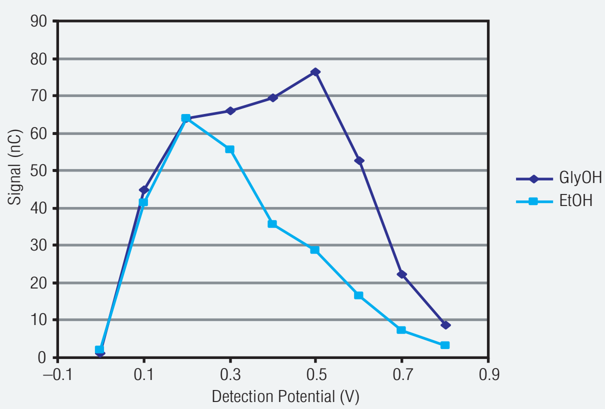
Waveform Optimization

Figure 4. Detection Response vs. Detection Potential (E1)



Oxidation Potential (E2): 1.20 V; Reduction Potential (E3): –0.70 V

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Table 1. Effect of Oxidative Potential (E2 or Step 1 "Cleaning Cycle")

E2[a] (V)	Peak Height (nC)		Peak Asymmetry		Lifetime[b] (Days)
	Glycerol	EtOH	Glycerol	EtOH	
1.00	43.10	12.15	1.83	2.52	11
1.10[c]	45.40	12.91	1.86	1.96	11
1.20	47.02	13.92	2.09	1.76	~7
1.30	49.26	14.74	2.30	1.93	5–6
1.40	49.03	14.82	1.98	1.73	~3
1.50	50.05	16.56	1.83	1.17	N. D.
1.60	49.39	15.48	1.96	1.66	<1

[a] In all runs, E1s and E3s are kept at 0.45 and –0.70 V, respectively.
[b] The lifetime was defined as a time interval required to dissolve the platinum layer under chromatographic detection conditions.
[c] Optimal conditions.

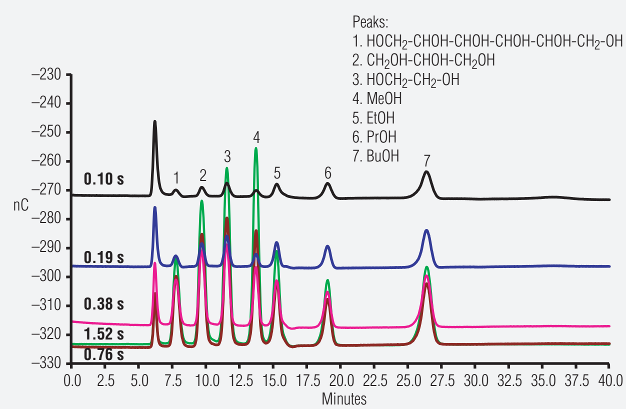
Table 2. Effect of Reductive Potential (E3 or Step 2 "Cleaning Cycle")

E3[a] (V)	Peak Height (nC)		Peak Asymmetry		Noise (nC)
	Glycerol	EtOH	Glycerol	EtOH	
0.20	57.33	16.07	2.82	1.79	0.210
0.00	51.24	18.62	2.70	1.86	0.180
–0.20[b]	47.71	18.54	2.48	1.52	0.147
–0.40[b]	54.04	22.06	2.41	2.07	0.148
–0.50	52.37	22.66	2.42	2.07	0.151
–0.60	44.73	21.23	2.38	2.12	0.156
–0.80	44.55	22.73	2.51	2.11	0.143

[a] Waveform conditions: detection potential (E1) is 0.45 V; Oxidation cleaning potential (E2) is 1.20 V.
[b] Optimal conditions.

Figure 5. Varying Duration of Step 1 of the "Cleaning Cycle"

Concentrations: 50 ppm all analytes (except butanol: 100 ppm)



Cleaning Time (s)	Response (nC, GlyOH)	Ratio of S/N (GlyOH)
0.10	3	52
0.19	8	93
0.38	26	233
0.76	39	351
1.52	49	549

Total Cleaning Times: 1.52, 0.76, 0.38, 0.19 and 0.10 s
Total Waveform Times: 1.83, 1.07, 0.69, 0.50 and 0.41 s

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Table 3. Optimized Waveform[a]		
Time (s)	Potential (V)[b]	Integration
0.00	0.30	
0.29	0.30	Start
0.31	0.30	End
0.32	1.15	
0.66	1.15	
0.67	–0.30	
1.06	–0.30	
1.07	0.30	

[a] RSD (%, electrode-to-electrode): Glycerol (3.46) and EtOH (12.35) with the optimized waveform
[b] Versus Ag/AgCl

ANALYTICAL PERFORMANCE OF DISPOSABLE PT ELECTRODES

Figure 6. Long-Term Stability: Optimized Waveform

Standards: 50 ppm

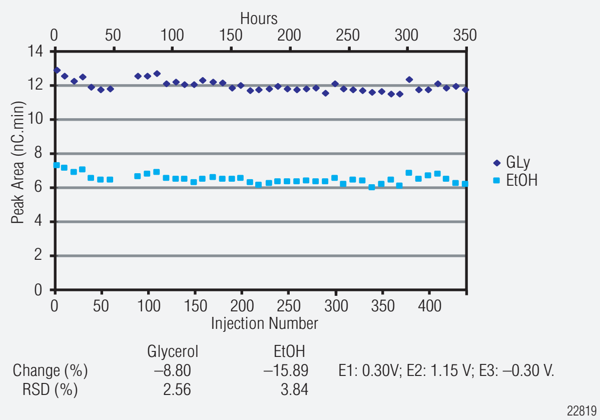


Table 4. Calibration Results			
Alcohol	Electrode Type	Range (ppm)	Correlation Coefficient[a]
Glycerol	Non-disposable	0.5–100	1.0000
	Disposable	0.5–100	0.9995
Ethanol	Non-disposable	1–500	0.9996
	Disposable	1–500	0.9998

[a] Quadratic fit

Table 5. Limits of Detection			
	Conventional Waveform	Optimized Waveform	
Alcohol	ED 40 Pt (ppm)	ED 40 Pt (ppm)	Disposable Pt (ppm)
Glycerol	0.54	0.20	0.10
Ethanol	1.63	0.51	0.25

SEPARATION AND DETECTION METHODS

Figure 7. Glycols

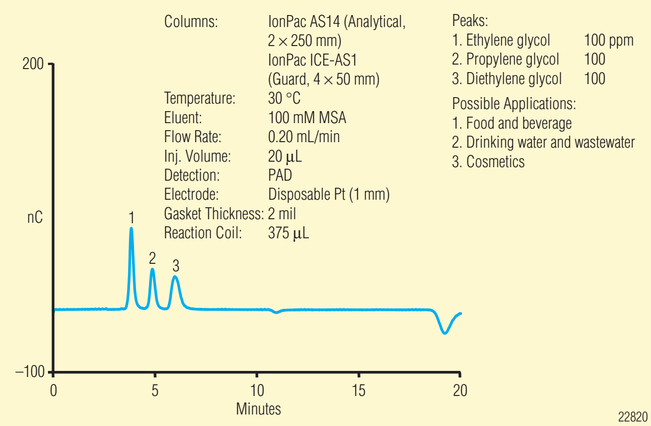


Figure 8. Alcohols

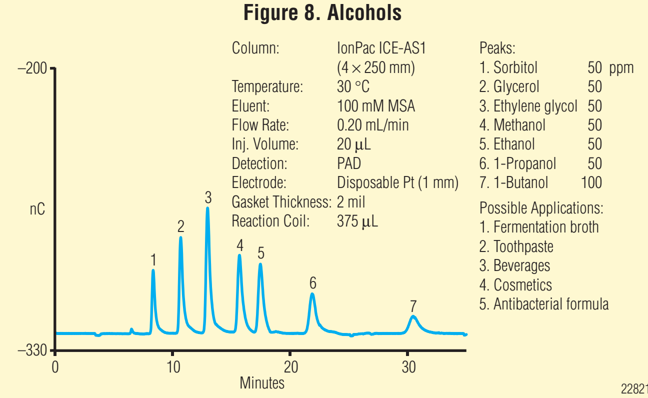


Figure 9. Formic Acid

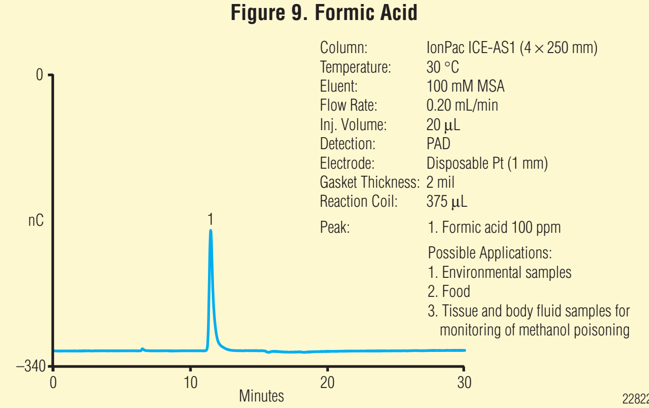


Figure 10. Cyanide and Azide

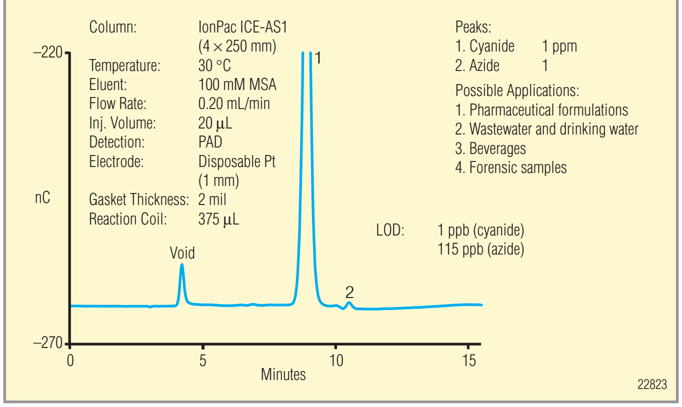


Figure 13. Red Wine Sample

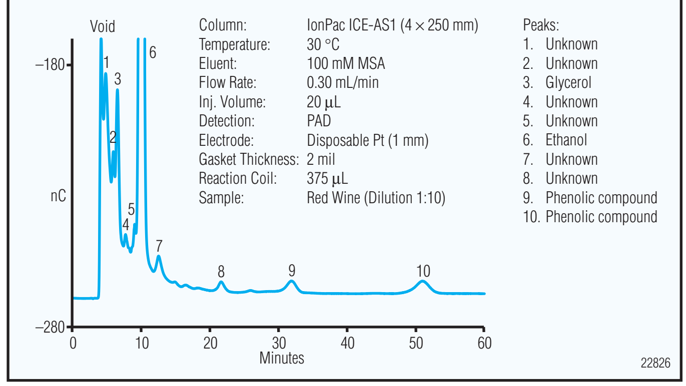


Figure 11. Phenol in an Alcohol Mixture

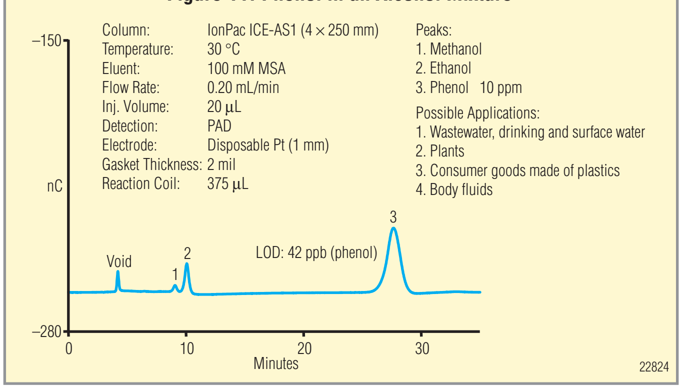
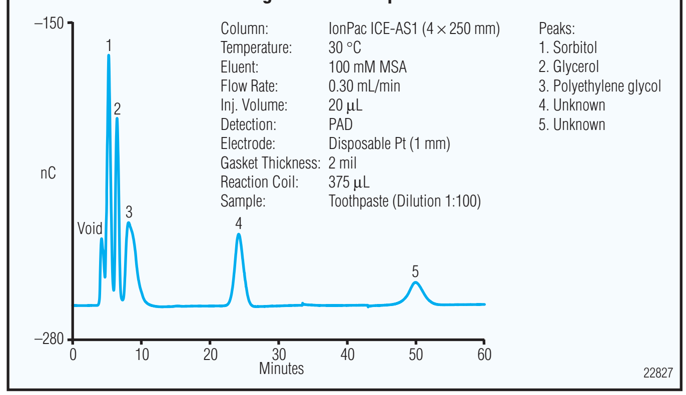
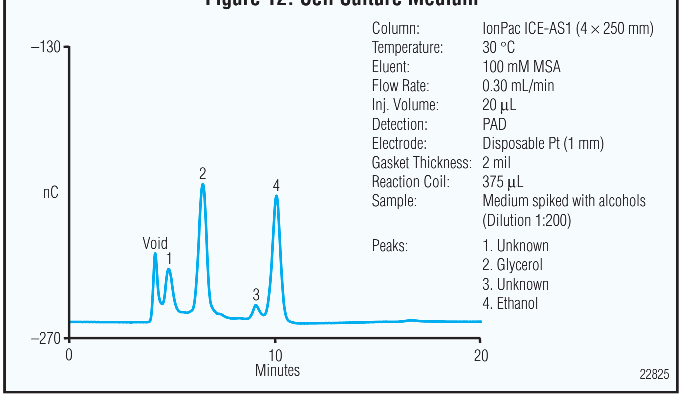


Figure 14. Toothpaste



APPLICATIONS

Figure 12. Cell Culture Medium



Conclusions

- Developed a fabrication process for manufacturing disposable Pt electrodes
  - Excellent electrode-to-electrode reproducibility
  - Faster start-up
  - No polishing and reconditioning
- Optimized a waveform for disposable and non-disposable Pt electrodes
- Improved analytical performance for determining alcohols and other compounds (e.g., cyanide and azide) in acidic eluent

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