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The Use of Narrow Gap Line Microelectrodes as Sensitive and
Species Selective Gas Chromatographic Detectors

by

R. Brina and S. Pons

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Department of Chemistry
University of Utah
Salt Lake City, UT 84112

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ABSTRACT

In this work we describe a new microelectrode assembly and its use as a sensitive electrochemical gas chromatographic detector. The conditions of operation of this device, i.e. pretreatment of the microelectrode surface, applied potential, and signal-to-noise ratio were studied in order to achieve maximum sensitivity and reproducibility. Condensation of the analyte in a thin gap between two parallel line microelectrodes comprising the electrochemical cell is considered to be the factor determining the sensitivity of this device.

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THE USE OF NARROW GAP LINE MICROELECTRODES AS SENSITIVE
AND SPECIES SELECTIVE GAS CHROMATOGRAPHIC DETECTORS.

Rossella Brina and Stanley Pons*
Department of Chemistry
University of Utah
Salt Lake City UT 84112

* To whom correspondence should be addressed.

INTRODUCTION

We have reported previously (1,2) the use of microelectrodes as sensitive and selective detectors in gas phase applications and in liquid solutions of high resistance. Several other novel applications of very small electrodes can be found in the recent literature (3-11). The selectivity of response of the microelectrode detector arises from the differences in the redox potential of the species under investigation. One then selects or filters response of various analytes by the applied potential to the electrochemical cell detector, or determines the species type by gas phase electroanalytical techniques, such as voltammetry (1). The small currents measured at microelectrodes (typically less than 10^{-10} A in dilute solutions) gives rise to several advantages. For instance, there are very small ohmic losses to the applied potential which means that electrochemical measurements can be carried out in highly resistive media (12-15). In addition, low polarization currents allow the use of two electrode systems, which eliminates the need for potentiostats. This latter advantage eliminates electronic noise in the measuring circuit. Typically, the only equipment required is a waveform generator and a current follower (14,16). Since the capacitive component to the total current is decreased compared to the faradaic component as the size of the electrode is decreased, sensitivity is enhanced compared to results at conventional larger electrodes.

The present work describes a new type of microelectrode assembly which operates by a different mechanism than that reported previously (1). We demonstrate its utility as an electrochemical detector for gas chromatography. The performance of the microelectrode detector described in (1) and of this new assembly is compared. A mechanism is suggested to explain the higher sensitivity values obtained with the new microelectrode assembly compared to those obtained

with the microelectrode detector in (1).

EXPERIMENTAL

REAGENTS

All organic solvents used were of analytical-reagent grade (Aldrich). Nanopure water was used. Tetra-n-butylammonium tetrafluoroborate (TBABF_4 , Chem-Biochem Research) was used as received.

APPARATUS

The microelectrode assembly used as the gas phase detector in this work is shown in Figure 1. It is a two electrode system consisting of two palladium microelectrodes (the working and the auxiliary-pseudoreference) mounted on a glass rod and separated by a small gap. The tip of a quartz glass rod (1mm o.d. at the tip) was polished flat with sandpaper and alumina. The glass rod was painted with undiluted Liquid Bright Palladium (Englehard Industries, Inc.), and the organometallic was thermally reduced to a palladium film at 625°C for 1h in a tube furnace. The palladium coating was then divided into two lateral halves by cutting with a fine metal blade; the cut extended down the side of the rod, horizontally across the tip, and up the other side of the rod. Electrical contact to the microelectrodes was obtained by painting the end of a fine insulated copper wire with colloidal silver paint onto the palladium metal coating, near the ends furthest from the tip of the rod. Once the solvent evaporates from the silver colloid, the contact is metallic and mechanically secure. The contacts were then insulated with epoxy resin. The potential applied to the microelectrode was controlled by a waveform generator (Hi Tek

Instruments, Model PPR1). A digital picoammeter (Keithley, Model 617), placed in series with the waveform generator and the electrochemical cell, was used to measure the currents. The microelectrode assembly was placed inside an aluminum Faraday cage in order to reduce capacitatively coupled noise. The gas chromatograph used in these experiments was a Hewlett-Packard Model 700. A short Teflon tube connected the gas outlet port to the microelectrode detector inside the Faraday cage. The tip of the microelectrode was inserted inside the Teflon tube. The column used in all of the experiments was Silicone OV-17 10% on ChromasorbW, and was 180cm x 3mm ID (80-100 mesh particle size). Helium was the carrier gas used, and was maintained at a constant flow rate of 30ml/min in all experiments.

PROCEDURE

The working microelectrode was maintained at +3.0V vs a palladium auxiliary microelectrode, unless otherwise stated. The measurements of the sensitivity and selectivity of the microelectrode detector were obtained by injecting 1 μ L portions of undiluted analytes into the chromatograph. The column and injection port temperatures were 80 and 170°C, respectively, for the analytes acetone, ethanol, methanol, cyclohexane, pentane, hexane, acetonitrile, methylene chloride, carbon tetrachloride, and ethyl acetate. The temperature at the gas chromatograph outlet port (1 mm from the microelectrode detector tip) was 100°C. The microelectrode detector itself was not temperature controlled, but was allowed to thermally equilibrate with the ambient for an hour before measurements were made. For all of the other solvents used, the column temperature was maintained at 120°C, the injection port at 190°, and the outlet port temperature was measured at 120°. For detection limit experiments, the microelectrode

response was studied under three different electrode surface conditions:

- (a) "as prepared", i.e. no intended surface modification.
- (b) the electrode tip was dipped into a 0.2M H₂SO₄ solution for 1 min.
- (c) the electrode tip was dipped into a 0.2M TBABF₄ solution for 1 min.

The electrode was then positioned inside the Faraday cage at the gas chromatograph exit port.

RESULTS AND DISCUSSION

Several classes of compounds were studied in order to determine the relative sensitivity and the selectivity of the microelectrode assembly as gas phase detector. Tables 1 and 2 show the responses obtained for 1 μ l injections of the different analytes. The column and injection port temperatures used for the compounds listed in Table 1 and Table 2 are listed in the experimental section. These responses are relative to the microelectrode as prepared. The second column in both Table 1 and 2 lists the ratio of the microelectrode response to the background current for the set of measurements relative to each analyte. Table 3 shows the responses for 1 μ l injections of the same analytes used in Tables 1 and 2, after the microelectrode had been treated with a 0.2M H₂SO₄ as described above. Generally the background noise of the detector appeared to be stable. Occasional fluctuations reflected in the data in the Tables are related to measurements made under conditions that were not optimized for signal to noise ratio. The treatment with sulfuric acid always leads to an increase in the response for each of the analytes, as shown in Table 3, column 3 (ratio between the response of the treated microelectrode and the untreated electrode). Generally, an increase in the background current is observed as a consequence of this treatment. However, a comparison between the signal-to-noise ratios for the two situations reveals that in most of the cases the signal-to-noise ratio is

also improved by the treatment with sulfuric acid. The effect of the sulfuric acid treatment is quite reproducible over a 12h period of continuous operation. The treatment was repeated daily in order to assure good reproducibility of the data (better than 5%). The treatment with sulfuric acid does not affect the stability or the reproducibility of the palladium microelectrode detector, which was not the case with the electrode described in (1). Under normal conditions of operation, the detector described herein is expected to last several hundreds of hours minimum.

The following experiments were carried out in order to assess the sensitivity of the palladium electrode assembly. 1 μ l injections of dilute cyclohexanone solutions in acetone were analyzed using different electrode pretreatments and at the same applied potential. Table 4 lists the detection limits observed for cyclohexanone and for the other compounds tested. We define herein the detection limits as the concentration that gives an average signal three times the background noise level. From this definition and from the values of the slope of the response vs. injected concentration plot for the analyzed species, the value of the detection limits in Table 4 were calculated. For all the compounds listed in Table 4, the lowest detection limits and the widest linearity ranges were obtained when the electrode had been pretreated with sulfuric acid as described.

Dilute aniline solutions in acetone were analyzed at two different electrode potentials with the same electrode pretreatment. A higher applied potential in this case causes a lower detection limit (Table 4). However, the difference in the two detection limits is not significant (10%) for a change in potential of 2V

Figure 2 shows the electrode response variation with the applied potential.

for $1\mu\text{l}$ injections of a 1% aniline solution in acetone. As the applied potential is increased, the electrode response increases. However, the background current (Table 5, column 2) and the noise (Table 4) tend to increase in this system as the potential is increased. This is responsible for the relatively small decrease in the detection limits observed for aniline as the potential increases.

The performance of the palladium electrode assembly is notably improved compared to that of the microelectrode detector described in (1). In Table 6 the responses of the two electrodes to various analytes are compared. Generally, the new electrode described in this paper shows higher responses (10 to 1000 times higher) and higher signal-to-noise ratios (compare Table 6 and Table 3) than the microelectrode described in (1). These marked improvements are responsible for the lower detection limits (45 to 87% gain) observed with parallel line palladium electrode assembly.

The higher sensitivity of this electrode assembly treated with sulfuric acid, compared to the sensitivity of the microelectrode in (1) can be explained in terms of the entrapment of sulfuric acid electrolyte in the narrow gap between the two line microelectrodes. The analyte from the chromatograph dissolves in this thin layer, and undergoes electron transfer at the electrodes. After the slug of analyte has been exhausted, the oxidized products in the thin layer electrolyte is rapidly extracted by the dry helium carrier gas at elevated temperature. Attempts to activate the surface between the electrodes of the detector described in (1) also resulted in enhanced detection, but the response was not reproducible and was unstable due to the lack of a well defined and stable cell geometry which results in a depletion of the electrolyte due to convection of the electrolyte away from the electrodes.

The electrochemical detector has the advantage that enhanced selectivity can

be obtained by accurate choice of the potential applied to the electrode. This has been discussed previously (1). Figure 3 shows the electrode response to a 1 μ l injection of a 50% toluene - 50% triethylamine solution at different applied potentials. The column temperature was 80°C, the injection port temperature was 170°C and the carrier gas flow rate was 30ml/min. As also observed in (1), the toluene response depends more on the applied potential than the triethylamine response, leading to a crossing of the two curves at low potentials. The Figure demonstrates therefore that it is possible to analyze a mixture in the gas phase for speciation by voltammetry at this detector. Similarly, mixtures of more than 2 analytes can be investigated; these results will be presented elsewhere. The nature of the inverted region is under continued investigation.

Figures 4 and 5 show typical chromatograms obtained at the thermal conductivity detector and at the palladium microelectrode detector. Figure 4 shows the chromatogram of a 50% triethylamine - 50% toluene solution (V/V); the column temperature was 80°C and the injection port was at 170°C. The outlet port was measured at 100°C. Figure 5 shows the chromatograph of a mixture of 30% toluene, 30% o-xylene, and 40% cyclohexane (V/V). The column temperature was 90°C and the injection port was at 190°C. The outlet port was measured at 120°C. The response times for the two detectors are essentially the same.

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Table 1. Response of the Palladium Electrode Detector (a).

Compound ^(b)	Response for electrode no surface treatment (pA)	Signal ^c Noise/1000	Retention Time, min
Acetone	10.32	4.0	0.44
Ethanol	436000	800	0.36
Methanol	599000	950	
Cyclohexane	0.67	1.1	0.72
Pentane	0.31	0.50	
Hexane	0.2	0.33	
Acetonitrile	25580	190	0.44
Methylene Chloride	2.33	3.3	0.76
Carbon Tetrachloride	0.82	1.1	0.76
Ethyl Acetate	85.19	11	

(a) Injections of 1 μ L undiluted material.

(b) Column temperature=80°C; Injection port temperature=170°C; Outlet port temperature=100°

(c) Assuming shot-noise limited, and 300ms time constant current measurements

Table 2. Response of the Palladium Electrode Detector (a).

Compound ^(b)	Response for electrode no surface treatment (pA)	Signal ^e Noise/1000	Retention Time, min ^c
Aniline	160	15	6.04 ^c
Butyl Alcohol	49300	270	
Cyclohexene	6.3	3	
Cyclohexanone	2310	590	4.52
Heptane	1.17	0.56	
Methylamine (40% in water)	344700	720	0.28 ^d
Triethylamine	6.57	590	0.44 ^d
Toluene	3.09	1.5	1.32
o-Xylene	1.83	0.75	3.48
(1,2,4)-Trimethylbenzene	0.97	0.37	7.4
Ethylbenzene	6.18	2.9	2.4
Chlorobenzene	110.7	10	
Trichloroethylene	101.6	9.2	
Water	59000	300	0.36

(a) Injections of 1 μ l undiluted material.

(b) Column temperature=120°C; Injection port temperature=190°C; Outlet port temperature=120°

(c) Column temperature=80°C; Injection port temperature=170°C; Outlet port temperature=100°

(d) Column temperature=90°C; Injection port temperature=170°C; Outlet port temperature=100°

(e) Assuming shot-noise limited, and 300ms time constant current measurements

Table 3. Response of the Palladium Electrode Detector^(a).

Compound ^(b)	Response after treatment w/H ₂ SO ₄ ^(c) (pA)	Signal ^d Noise/1000	Ratio <u>Treated Elec.</u> <u>Not Treated</u>
Aniline	5000	870	31.2
Acetone	2309	400	223.7
Ethanol	1150000	1300	2.6
Methanol	1510000	1500	2.5
Butyl Alcohol	2680000	2000	54.4
Cyclohexane	3.57	2.3	5.3
Cyclohexene	29.98	19	4.8
Cyclohexanone	34200	230	14.8
Pentane	2.31	1.8	7.4
Hexane	4.48	2.6	22.4
Heptane	8.92	3.7	7.6
Methylamine (40% in water)	2478000	1900	7.2
Triethylamine	136.1	14	20.7
Toluene	132.41	14	42.8
o-Xylene	249	19	136
(1,2,4)- Trimethylbenzene	51	8.7	52.6
Ethylbenzene	207.4	18	33.6
Chlorobenzene	12600	137	113.8
Trichloroethylene	608	30	5.98
Water	1027000	1200	17.4
Acetonitrile	5070000	2800	198.2
Methylene Chloride	181.6	16	77.9

Table 3. Continued

Compound	Response after treatment w/H ₂ SO ₄	(pA)	<u>Signal</u> Noise	Ratio <u>Treated Elec.</u> Not Treated
Carbon Tetrachloride	30.5		6.8	37.2
Ethyl Acetate	520		28	6.1

- (a) Injections of 1 μ l undiluted material.
- (b) Gas chromatographic conditions as in Tables 1 and 2 for each compound.
- (c) The electrode was treated with 0.2M H₂SO₄ solution for 1min.
- (d) Assuming shot-noise limited, and 300ms time constant current measurements

Table 4. Detection Limits^(a) for the Palladium Electrode Detector.

Compound	Electrode treatment	Applied Potential (V)	Detection Limits (ppm)	Linearity ^(b)	Noise Level (pA)	Decades Covered ^(c)
Cyclohexanone ^(d)	none	+3.0	1260	0.97	0.07	1
Cyclohexanone ^(d)	0.2M H ₂ SO ₄	+3.0	21	0.9999	0.34	4
Cyclohexanone ^(d)	0.2M TBABF ₄	+3.0	47	0.9996	0.07	1.5
Aniline ^(e)	0.2M H ₂ SO ₄	+3.0	14	0.9999	0.06	3
Aniline ^(e)	0.2M H ₂ SO ₄	+5.0	12.5	0.9999	0.1	3.5
Toluene ^(f)	0.2M TBABF ₄	+3.0	260	0.998	0.07	2
Acetonitrile ^(g)	0.2M TBABF ₄	+2.5	380	0.997	0.03	1.5
Methanol ^(h)	0.2M H ₂ SO ₄	+3.0	44	0.997	0.02	2.5
Ethanol ⁽ⁱ⁾	0.2M H ₂ SO ₄	+3.0	31	0.9999	0.02	3

- (a) Concentration that gives an average signal three times the noise level
 (b) Regression coefficient of the electrode response vs. concentration plot
 (c) Concentration range for the regression coefficient listed, in decades
 (d) 1 μ l injection of cyclohexanone solutions in acetone; Column temperature = 120°C; Outlet port temperature = 120°
 (e) 1 μ l injection of aniline solutions in acetone; Column temperature = 120°C; Outlet port temperature = 120°
 (f) 1 μ l injection of toluene solutions in o-xylene; Column temperature = 120°C; Outlet port temperature = 120°
 (g) 1 μ l injection of acetonitrile solutions in butyl alcohol; Column temperature = 80°C; Outlet port temperature = 100°
 (h) 1 μ l injection of methanol solutions in butyl alcohol; Column temperature = 80°C; Outlet port temperature = 100°
 (i) 1 μ l injection of ethanol solutions in butyl alcohol; Column temperature = 80°C; Outlet port temperature = 100°

Table 5. Palladium Electrode Response with Applied Potential for 1 μ l injection of a 1% Aniline solution in Acetone.

Applied Potential (V)	Aniline Response (pA)	<u>Signal</u> ^a Noise/1000
7.0	55	9.1
6.5	50	8.7
6.0	47	8.3
5.0	37.6	7.5
4.0	29.98	6.7
3.0	20.97	5.6
2.0	10.44	4.0
1.0	6.71	3.2
0.5	1.13	1.3
0.0	-3.3	2.2

(a) Assuming shot-noise limited, and 300ms time constant current measurements

Table 6. Comparison between the Palladium Electrode Assembly and the Microelectrode Detector (1) performances.

Compound	Ratio $\frac{\text{Palladium Response}}{\text{Microelectrode Response}}$ ^(a)	Signal ^(b) Noise/1000	Detection Limits ^(b) (ppm)	Detection Limits Gain ^(c)
Acetone	182.4	4.36		
Ethanol	12.8	367		
Cyclohexane	238	0.15		
Cyclohexanone	30.4	41		
Methylamine (40% in water)	14.7	503	160	87%
Triethylamine	63.6	1.8		
Toluene	2.3	9	490	46%
o-Xylene	15.4	5		
(1,2,4)- Trimethylbenzene	19.7	2		
Ethylbenzene	2728.9	0.4		
Water	23.5	256		
Acetonitrile	363.7	145	690	45%
Methylene Chloride	0.3	30		
Carbon Tetrachloride	97.8	0.7		
Ethyl Acetate	3.8	14		
Aniline	0.4	130	82	83%

- (a) Ratio of the response of the palladium electrode treated with sulfuric acid to the response of the microelectrode in (1) treated with TBABF₄. Chromatographic conditions are the same for each compound in each set of measurements.
- (b) Microelectrode in (1) treated with TBABF₄, assuming shot-noise limited, and 300ms time constant current measurements
- (c) Gain in the detection limits for the palladium electrode used in this work over that used in (1).

FIGURE CAPTIONS

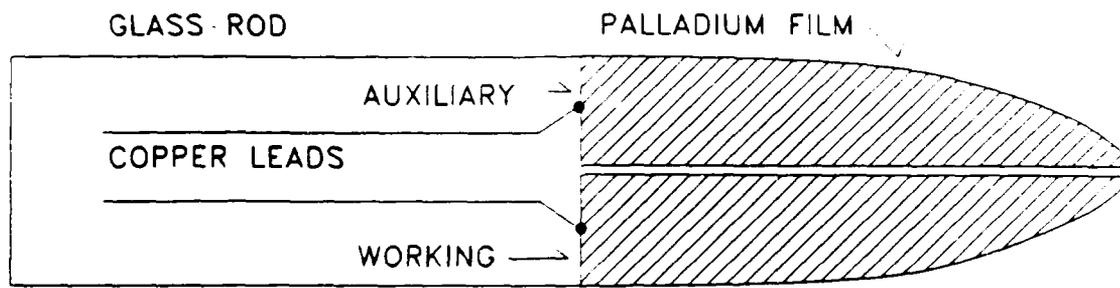
Figure 1. Palladium electrode assembly.

Figure 2. Electrode response vs. applied potential for $1\mu\text{l}$ injection of 1% aniline solution in acetone. Aniline response.

Figure 3. Electrode response vs. applied potential for a $1\mu\text{l}$ injection of 50% toluene- 50% triethylamine solution. (x) triethylamine; (o) toluene response. Column temperature= 80°C , injection port temperature= 170°C .

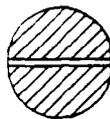
Figure 4. (a) Palladium microelectrode detector (b) thermal conductivity detector responses for $1\mu\text{L}$ injections of a solution of 50% triethylamine (1) - 50% toluene solution (2) (V/V); the column temperature was 80°C and the injection port was at 170°C . The outlet port was measured at 100°C . Potential at the working electrode was +3.0V vs the auxiliary. The total time elapsed was 2.2 min.

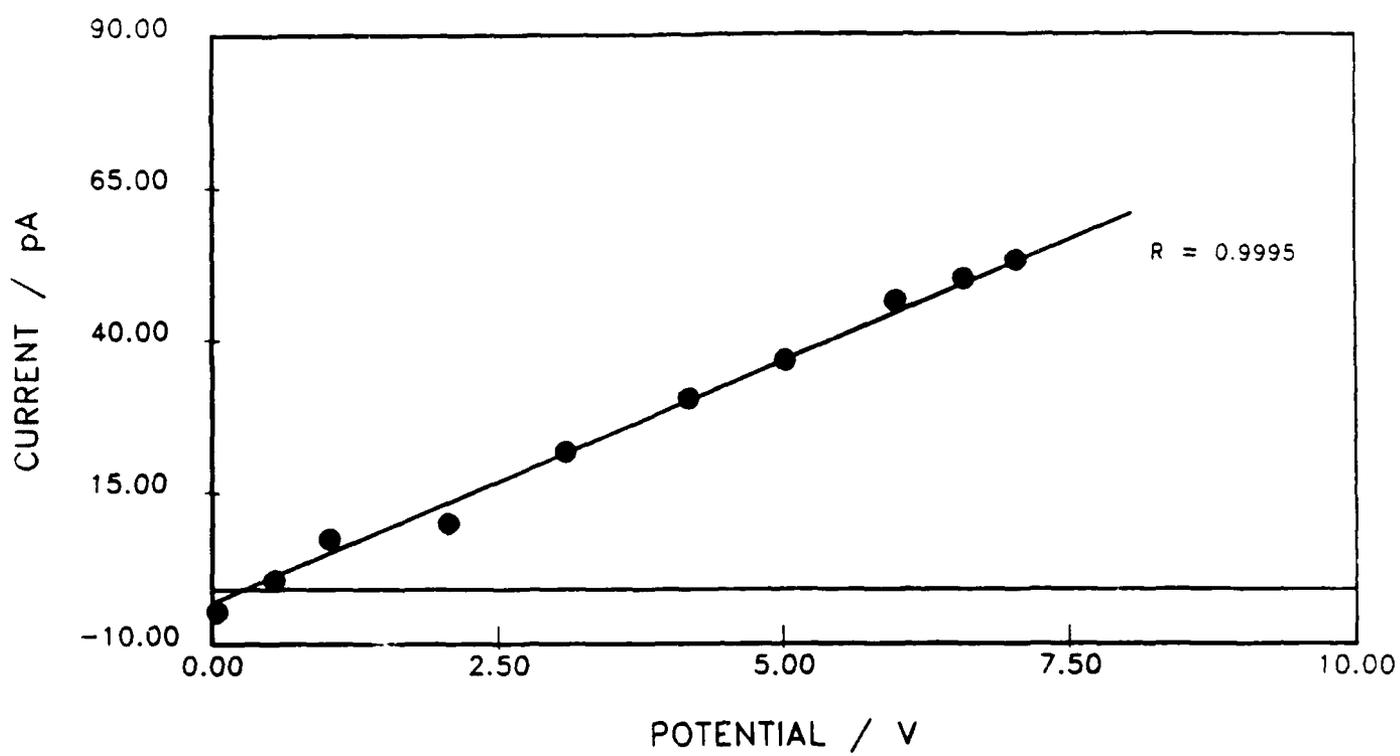
Figure 5. (a) Palladium microelectrode detector (b) thermal conductivity detector responses for a $1\mu\text{L}$ injections of a mixture of 30% toluene (1), 30% o-xylene (2), and 40% cyclohexane (3) (V/V). The column temperature was 90°C and the injection port was at 190°C . The outlet port was measured at 120°C . The peak shapes for each detector are apparently the same. The total time elapsed was 11.2 min.

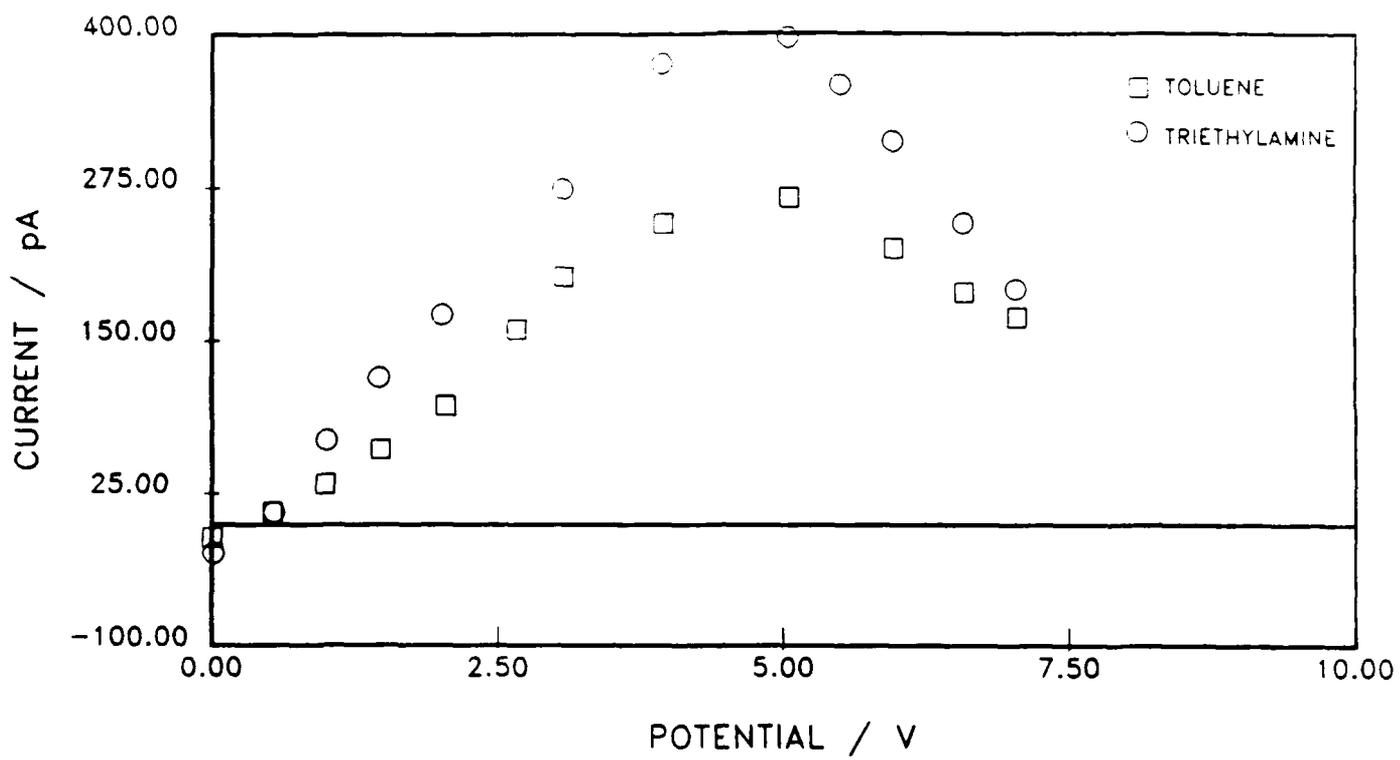


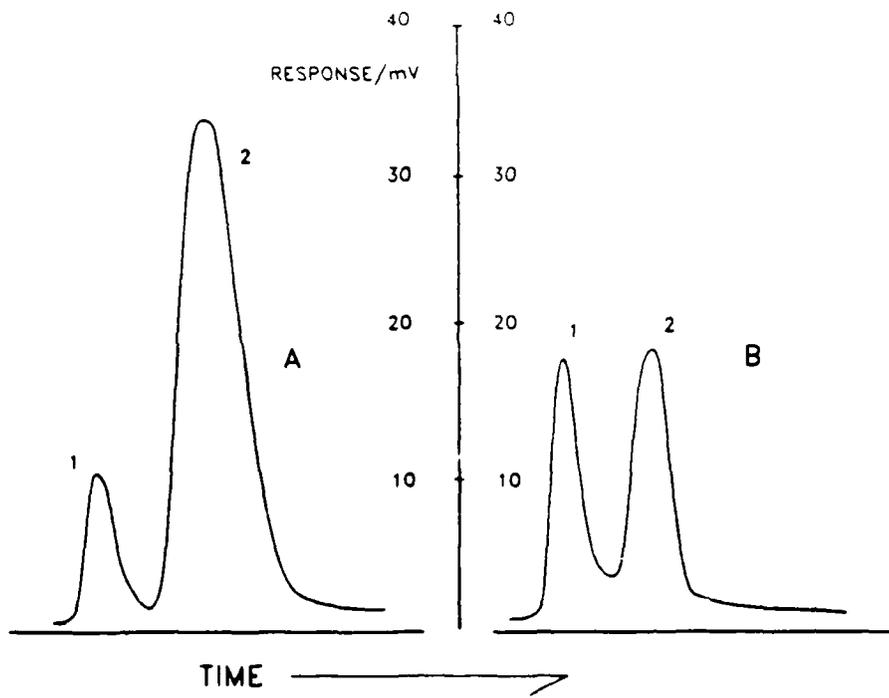
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Provo, UT 84602

Dr. Stanley Pons
~~Department of Chemistry~~
University of Utah
Salt Lake City, UT 84112

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Honeywell, Inc.
10701 Lyndale Avenue South
Bloomington, MN 55420

Dr. J. Foos
EIC Labs Inc.
111 Downey St.
Norwood, MA 02062

Dr. Neill Weber
Ceramatec, Inc.
163 West 1700 South
Salt Lake City, UT 84115

Dr. Subhash C. Narang
SRI International
333 Ravenswood Ave.
Menlo Park, CA 94025

Dr. J. Paul Pemsler
Castle Technology Corporation
52 Dragon Ct.
Woburn, MA 01801

Dr. R. David Rauh
EIC Laboratory Inc.
111 Downey Street
Norwood, MA 02062

Dr. Joseph S. Foos
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Donald M. Schleich
Department of Chemistry
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 01

Dr. Stan Szpak
Code 633
Naval Ocean Systems Center
San Diego, CA 92152-5000

Dr. George Blomgren
Battery Products Division
Union Carbide Corporation
25225 Detroit Rd.
Westlake, OH 44145

Dr. Ernest Yeager
Case Center for Electrochemical
Science
Case Western Reserve University
Cleveland, OH 44106

Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, CA 93555

Dr. Ashok V. Joshi
Ceramatec, Inc.
2425 South 900 West
Salt Lake City, Utah 84119

Dr. W. Anderson
Department of Electrical &
Computer Engineering
SUNY - Buffalo
Amherst, Massachusetts 14260

Dr. M. L. Gopikanth
Chemtech Systems, Inc.
P.O. Box 1067
Burlington, MA 01803

Dr. H. F. Gibbard
Power Conversion, Inc.
495 Boulevard
Elmwood Park, New Jersey 07407

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ABSTRACTS DISTRIBUTION LIST, SDIO/IST

Dr. V. R. Koch
Covalent Associates
52 Dragon Court
Woburn, MA 01801

Dr. Randall B. Olsen
Chronos Research Laboratories, Inc.
4186 Sorrento Valley Blvd.
Suite H
San Diego, CA 92121

Dr. Alan Hooper
Applied Electrochemistry Centre
Harwell Laboratory
Oxfordshire, OX11 0RA UK

Dr. John S. Wilkes
Department of the Air Force
The Frank J. Seiler Research Lab.
United States Air Force Academy
Colorado Springs, CO 80840-6528

Dr. Gary Bullard
Pinnacle Research Institute, Inc.
10432 N. Tantan Avenue
Cupertino, CA 95014

Dr. J. O'M. Bockris
Ementech, Inc.
Route 5, Box 946
College Station, TX 77840

Dr. Michael Binder
Electrochemical Research Branch
Power Sources Division
U.S. Army Laboratory Command
Fort Monmouth, New Jersey 07703-5000

Professor Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton, Hants, SO9 5NH UK