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SEP 22 1998

ENGINEERING DATA TRANSMITTAL

Page 1 of 1

1. EDT 625711

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) TWRS Life Extension Equipment Engineering	4. Related EDT No.: 625711
5. Proj./Prog./Dept./Div.: 241-AZ-101 Corrosion Probe	6. Design Authority/ Design Agent/Cog. Engr.: G. L. Edgemon, Cog Engineer	7. Purchase Order No.: N/A
8. Originator Remarks: For release. Approval designators mandated by HNF-PRO-233		9. Equip./Component No.: 241-AZ-101 Corrosion Probe
		10. System/Bldg./Facility: 241-AZ-101
11. Receiver Remarks: 11A. Design Baseline Document? ☐ Yes ☒ No		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: N/A

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	HNF-3416		0	Tank 241-AZ-101 Prototype Corrosion Probe Two-Year Status Report	N/A	2	1	1

16. KEY

Approval Designator (F)	Reason for Transmittal (G)	Disposition (H) & (I)
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION
(See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN
		Design Authority									
		Design Agent									
1	1	Cog.Eng. G. L. Edgemon		9/21/98	R1-30						
1	1	Cog. Mgr. D. B. Smet	D B Smet	9-21-98	R1-56						
		QA									
		Safety									
		Env.									

18.	19.	20.	21. DOE APPROVAL (if required)
G. L. Edgemon 9/21/98 Signature of EDT Originator Date	S. H. Rifaey Authorized Representative Date for Receiving Organization	G. L. Edgemon D B Smet 9-21-98 Design Authority/ Cognizant Manager Date	Ctrl. No. N/A ☐ Approved ☐ Approved w/comments ☐ Disapproved w/comments

BD-7400-172-2 (05/96) GEF097

BD-7400-172-1

HNF-3416, Rev. 0

Tank 241-AZ-101 Prototype Corrosion Probe Two-Year Status Report

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U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: 625711 UC: 604
Org Code: 74711 Charge Code: N16B1
B&R Code: EW4010000 Total Pages: 64

Key Words: Electrochemical noise, corrosion monitoring, corrosion, pitting, stress corrosion cracking, localized corrosion, tank monitoring

Abstract: Document describes first two years of operation of 241-AZ-101 prototype electrochemical noise based corrosion monitoring system. Data and system status are presented.

Printed in the United States of America. To obtain copies of this document, contact: Document Control Services, P.O. Box 950, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

DATE:
HANFORD RELEASE
STA: 4
ID: 2
SEP 22 1998

9/22/98

Release Approval Date Release Stamp

Approved for Public Release

TANK 241-AZ-101 PROTOTYPE CORROSION PROBE TWO-YEAR STATUS REPORT

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EXECUTIVE SUMMARY

Corrosion monitoring of double-shell tanks at the site is currently provided by process knowledge and tank waste chemistry sampling. Tanks found to be within chemistry specification limits are considered to be safe from excessive corrosion damage. The recent discovery of five low hydroxide (out of corrosion specification) tanks at Hanford indicates that the current system of chemistry sampling is inadequate to adequately support corrosion control.

In an effort to improve corrosion monitoring and control, an electrochemical noise (EN) based corrosion monitoring system was successfully designed, fabricated and installed into double-shell tank 241-AZ-101 in August 1996. This system has collected over 50,000 data files and has operated reliably for approximately two years. At the time of its installation, it was the first system of its kind in the world. Since the time of its installation, two more advanced electrochemical noise based systems have been installed at Hanford - one in 241-AN-107 in September 1997 and one in 241-AN-102 in August 1998.

The 241-AZ-101 system monitors fluctuations in current and potential caused by corrosion occurring on an electrode array immersed in the tank waste and is capable of detecting the onset of pitting and stress corrosion cracking should tank waste conditions change to allow these mechanisms to occur. Pitting and stress corrosion cracking are the two most likely corrosion failure modes for DSTs at Hanford. The system also supports the use of linear polarization resistance testing for determination of uniform corrosion rate. By monitoring and analyzing the data from these techniques, dominant corrosion mechanisms in 241-AZ-101 have been determined.

Large flush water additions to 241-AZ-101 induce pit initiation and growth. Extensive pitting has been observed following condensate and flush water additions made on 10/3/96, 10/24/96, 12/18/96, 1/16/97, 2/12/97, 4/28/97, 8/16/97, and 11/25/97. Each of these water additions was over 6,500 gal (24,600 L) in volume. Raw data prior to water additions in all cases is typical of uniform corrosion in passive systems. Raw data collected after each large water addition is typical of pit initiation and growth. Pitting transients persisted for a few weeks after the water additions in each case. Reducing the delivery rate of the water additions to the tank would likely reduce the tendency to induce pit initiation and growth.

Data collected during normal operation of the tank (not following water additions) indicate that uniform corrosion is the dominant corrosion mechanism in 241-AZ-101.

Data indicative of pit initiation and growth following large water additions to tank 241-AZ-101 at the Hanford site are consistent with previously published predictions of pitting behavior in waste tanks at other nuclear waste storage facilities.

During uniform corrosion (verified by inspection of raw EN data), corrosion rates determined from both LPR measurements and EN data were less than 1 mpy.

Data collected from the Hanford Site prototype corrosion probe indicates that an EN/LPR based corrosion monitoring system can be successfully applied to nuclear waste tank environments.

INTRODUCTION AND BACKGROUND

The Hanford Site has 177 underground waste tanks that store approximately 253 million liters of radioactive waste from 50 years of plutonium production [1]. Twenty-eight (28) tanks have a double shell and are constructed of welded ASTM A537-Class 1 (UNS K02400), ASTM A515-Grade 60 (UNS K02401), or ASTM A516-Grade 60 (UNS K02100) material. The inner tanks of the double-shell tanks (DSTs) were stress relieved following fabrication. One hundred forty-nine (149) tanks have a single shell, also constructed of welded mild steel, but not stress relieved following fabrication. Tank waste is in liquid, solid, and sludge forms. Tanks also contain a vapor space above the solid and liquid waste regions. The composition of the waste varies from tank to tank but generally has a high pH (>12) and contains sodium nitrate, sodium hydroxide, sodium nitrite, and other minor radioactive constituents resulting from plutonium separation processes [1-4]. Leaks began to appear in the single-shell tanks shortly after the introduction of nitrate-based wastes in the 1950s. Leaks are now confirmed or suspected to be present in a significant number of single-shell tanks [1]. The probable modes of corrosion failures are reported as nitrate stress corrosion cracking (SCC) and pitting [2].

Corrosion monitoring of DSTs is currently provided at the Hanford Site by process knowledge and tank waste chemistry sampling [1-4]. Tanks found to be within chemistry specification limits are considered to be safe from excessive corrosion damage. The recent discovery of five low hydroxide (out of corrosion specification) tanks at Hanford indicates that the current system of chemistry sampling is inadequate to support corrosion control. Tank samples are infrequent and analyses are difficult and expensive. Furthermore, waste streams that are exempt from the corrosion control specifications complicate process knowledge. In-tank, real-time measurement of waste corrosivity is needed to provide an acceptable level of corrosion control information.

Available technologies such as the electrochemical noise (EN) technique for corrosion monitoring have progressed to a point where it is now feasible to detect and monitor the forms of corrosion most likely to affect Hanford DSTs [5-22]. Previous efforts to monitor internal corrosion of high-level nuclear waste tank systems have included the linear polarization resistance (LPR) and electrical resistance techniques [23, 24]. These techniques are most effective for monitoring uniform corrosion, but are not well suited for detection of localized corrosion. The Savannah River Site (SRS) investigated the characterization of electrochemical noise (EN) for monitoring waste tank corrosion in 1993, but the tests were not conclusive [25]. The SRS effort has recently been revived and additional testing is underway. A two-year laboratory study was launched at Hanford in 1995 to provide a technical basis for applying EN based corrosion monitoring systems to nuclear waste tanks [26-28]. Personnel at the Hanford Site, Oak Ridge National Laboratory, Pacific Northwest National Laboratory, and several instrumentation manufacturers participated in the program. This testing program conclusively demonstrated the ability to use EN based corrosion monitoring systems to detect and discriminate between forms of localized corrosion and led to the development and deployment of a prototype corrosion monitoring system into DST 241-AZ-101 in August 1996. The successful operation of the prototype led to the development and deployment of two more advanced EN based systems in DSTs 241-AN-107 and AN-102 in September 1997 and August 1998 respectively. This report presents an extensive review of data collected from the 241-AZ-101 prototype system over its first two years of operation.

241-AZ-101 SYSTEM DESIGN AND CONFIGURATION

The 241-AZ-101 corrosion monitoring system is designed, like most EN based corrosion-monitoring systems, to measure instantaneous fluctuations in corrosion current and potential between three nominally identical electrodes (a working, a counter, and a pseudo-reference electrode) of the material of interest immersed in the environment of interest. Time-dependent fluctuations in corrosion current between the working and counter electrodes are described by electrochemical current noise. Time-dependent fluctuations of the difference in the corrosion potential between the working/counter electrode assembly and the pseudo-reference electrode are described by electrochemical potential noise. Since a zero resistance ammeter (ZRA) electrically joins the working and counter electrodes, potential differences are measured between the working/counter electrode assembly and the pseudo-reference electrode. It has been shown that each type of corrosion phenomenon presents a unique relationship between corrosion current and potential transients in the temporal data [5-22, 26-28]. Other methods of analysis involve transforming temporal data to the frequency domain for analysis [29]. As of the time of the preparation of this report, no frequency analysis of the EN data from the 241-AN-107 system has been performed or is expected. However, statistical analysis techniques have been employed. The system also facilitates the use of the Tafel and LPR techniques to collect uniform corrosion rate information.

The following design goals were established for the prototype probe system:

- Provide at least two years of service
- Fit through 10 cm diameter riser
- Facilitate remote data acquisition and system control
- Facilitate decontamination by minimizing liquid retention

The probe system was designed to operate under the following conditions:

- Temperature ranges up to 100°C
- Liquid phase pH ranges from 7 to 14
- Radiation levels up to 1000 R/hr
- Liquid phase flow rates up to 1.0 m/s

A schematic diagram of the corrosion monitoring system is shown in Figure 1. The prototype corrosion probe is constructed from 3.8-cm diameter AISI 304L stainless steel (UNS 30403) pipe for extended service in the waste tank environment. It fits through a nominal 10.2-cm diameter tank riser and is approximately 10 meters long.

The probe has electrode arrays at the 3.9-m, 8.8-m, and 9.9-m depths from the top of the riser. The upper two electrode arrays are positioned to monitor vapor phase corrosion. The lowermost array was initially positioned at a depth of 55 cm below the waste surface. Due to evaporative losses from the waste tank over the last few years, the lowermost electrode array is now approximately 20 cm below the waste surface. The probe tree assembly prior to installation is shown in Figure 2. Each electrode array consists of three nominally identical C-ring (ASTM G-38) electrodes constructed of archived ASTM A537-Class 1 tank steel to best represent actual tank wall material. A detail of an electrode array is shown in Figure 3. The working (center) electrode in the liquid phase array was pre-cracked by cyclic fatigue and strained beyond the proportional limit just prior to immersion in the waste. The other two liquid phase electrodes were not strained or pre-cracked. The working electrodes of the vapor space arrays were not pre-cracked, but were strained beyond the proportional limit prior to installation.

A 10 conductor shielded data cable extends through the length of the interior of the sealed pipe. At each electrode array, three conductors are removed from the shielding and attached to the three electrodes, one per electrode. A commercially available glass to metal seal is used to penetrate the probe tree pipe wall while maintaining electrical isolation between the electrodes and the pipe wall. Electrodes are isolated from the glass to metal seals through the use of peroxide cured ethylene propylene (EPDM) gaskets suitable for radiation environments. The shielded cable terminates at the top to the probe tree assembly in a weather tight box. Approximately 24 meters of above ground cable runs from the top of the probe to the corrosion monitoring instrumentation. The above ground cabling is shielded from electrical interference with driven Faraday shields produced by the corrosion monitoring instrumentation. A schematic of the entire system is shown in Figure 4.

The corrosion monitoring instrumentation utilizes a Gamry Instruments CMS100 electrochemical measurement system with an eight channel multiplexer and associated software.[1] Galvanic corrosion operating software for this system was customized and optimized for EN data collection. Data are collected sequentially on the electrode arrays using three channels of the multiplexer. Potential and current measurements are recorded once per second on the active array. Data are typically collected for 600 seconds per channel. Post-collection data analysis is performed using internally developed statistical analysis software and Microsoft Excel.[2] Data acquisition began following electronics package installation on August 8, 1996. With the exception of occasional power failures and instrument malfunctions, data acquisition on the single channel immersed in the supernate has been continuous since installation. Data acquisition was terminated on the vapor space channels in April 1997 after it became apparent that the EN system electronics did not have the necessary level of potential noise sensitivity to record meaningful information from electrodes exposed in the low electrolyte levels in the vapor space. This report will concentrate on the corrosion data collected from the single C-ring channel immersed in the supernate.

SUPERNATE SUMMARY STATISTICAL DATA

Summary statistical data for the first two years following probe installation are shown in Figures 5 through 13. Although it is not strictly possible to distinguish between forms of corrosion using statistical data alone, statistical analysis of the raw data files is useful in identifying time periods of change in corrosion behavior. By limiting preliminary raw data analysis to files associated with large changes in the summary statistical data, time spent on data analysis was greatly reduced. Gaps in the summary statistical data indicate loss of data due to equipment disturbance, maintenance, and power failures.

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[1] Gamry and CMS100 are trademarks of Gamry Instruments, Inc., Willow Grove, Pennsylvania.

[2] Microsoft and Excel are registered trademarks of Microsoft Corporation, Redmond, Washington.

Water Additions to 241-AZ-101

During the two-year monitoring period, the largest changes in tank corrosion behavior were the result of raw or inhibited water additions to the tank. Historically, water has been added to the tank during thermocouple removal operations and to replace evaporative losses due to the high heat load associated with aging nuclear waste. Tank volume over the course of the two-year monitoring period is shown in Figure 5. Table 1 summarizes the water additions evident in Figure 5.

Mean Current

Mean current is shown in Figure 6. Mean current ranged from approximately 3 μA immediately following installation to approximately -1 μA over the course of operation. Mean current decreased over the first few months of operation and eventually stabilized at a slightly positive value. Mean current levels temporarily reached values of up to ±10 μA during water additions made in October 1996 and February 1997. The effects of other water additions can also be seen. The average value of mean current over the first two years of operation was 0.24 μA. The sign convention on the equipment is set so that a positive current is recorded by the 241-AZ-101 monitoring system when the working electrode is anodic with respect to the counter electrode. In most cases, mean current temporarily decreased immediately following water additions. This effect is thought to be due to waste oxygenation and mixing causing a temporary increase in passive film thickness. Water injection likely forces waste with high hydroxide concentrations from deep within the tank upward to mix with waste with lower hydroxide concentrations near the surface. Waste concentration eventually equilibrates and mean current levels return to pre-water addition levels.

For approximately two months following installation, the trend and behavior of the mean current data were typical of carbon steel electrodes immersed in a high pH, passivating tank waste solution [26-28]. The initial slope of the mean current curve is related to the direction of corrosion current flow due to initial differences in potential between the counter and working electrodes. Since these electrodes are connected to each other through a zero resistance ammeter (ZRA), a potential difference between the two electrodes will set up a current flow between the two electrodes when immersed in a conductive solution.

Potential differences in electrodes made of the same material are caused by a variety of reasons including differences in surface finish, differences in grain size, differences in grain boundary chemistry, small variations in composition, differences in stress levels between electrodes, and other factors. Since only the working electrode is stressed, the working electrode should remain slightly more active than the other two electrodes (working electrode is more anodic with respect to unstressed electrodes). Based on the hardware/software settings on the 241-AZ-101 EN equipment, the mean current level should settle at a slightly positive value due to the difference in stress levels between the working and counter electrodes. However, as the passive state of the electrodes becomes more stable over time mean current flowing between the counter and working electrodes should approach zero. Barring any crack advance, pit initiation, or other electrode surface disturbance, passivation and equilibration of potential between electrodes will generally produce a slow movement in mean current toward a stable value near zero, as seen in Figure 6.

If mean current levels were to remain consistently positive, it could be assumed that the working electrode is corroding preferentially to the counter electrode and could be suffering from intergranular attack, a precursor for intergranular stress corrosion cracking (IGSCC) in carbon steels [26-28]. If the mean current levels were to stay consistently negative, it could be assumed that the counter electrode is corroding preferentially to the working electrode and could be suffering from intergranular or other localized attack. In either case, raw data must be examined before making a corrosion mechanism determination. With the exception of time periods immediately following large water additions, mean current data indicate that uniform corrosion is the dominant form of corrosion occurring during normal operation of 241-AZ-101. Based on previous laboratory studies, mean current data also indicate that large water additions to the waste tank temporarily induce localized corrosion in 241-AZ-101 [26-28]. However, raw data from the time periods immediately following water additions must be examined before the exact mechanism of corrosion can be established.

Mean Potential

Mean potential ranged from approximately -12 mV immediately following installation to approximately 1 mV over the course of operation. Mean potential increased over the first few months of operation and eventually stabilized at a slightly negative value. Mean potential levels temporarily reached values of approximately 20 mV and -30 mV during water additions made in October 1996 and February 1997. The effects of other water additions can also be seen. The average value of mean potential over the first two years of operation was approximately -3 mV. The sign convention on the equipment is set so that a negative potential is recorded by the 241-AZ-101 monitoring system when the working/counter electrode assembly is anodic with respect to the pseudo-reference electrode.

For approximately two months following installation, the trend and behavior of the mean potential data were typical of carbon steel electrodes immersed in a high pH, passivating tank waste solution [26-28]. The initial slope of the mean potential curve is related to potential differences between the working/counter electrode assembly and the pseudo-reference electrode. Potential differences in electrodes made of the same material are caused by a variety of reasons including differences in surface finish, differences in grain size, differences in grain boundary chemistry, small variations in composition, differences in stress levels between electrodes, and other factors. Since only the working electrode is stressed, the working electrode should remain slightly more active than the other two electrodes. Because the working electrode is electrically linked to the counter electrode (through the ZRA), the counter/working electrode assembly is more active (on average) than the pseudo-reference electrode. Based on the hardware/software settings on the 241-AZ-101 EN equipment, the mean potential level should settle at a slightly negative value due to the difference in average stress levels between the working/counter electrode assembly and the pseudo-reference electrode. However, as the passive state of all three electrodes becomes more stable, potential differences will approach zero. Barring any crack advance, pit initiation, or other electrode surface disturbance, passivation and equilibration of potential between electrodes will generally produce a slow movement in mean potential from a more negative value toward a less negative value near zero, as seen in Figure 7.

If mean potential levels were to remain consistently negative, it could be assumed that the working electrode and is corroding preferentially to the pseudo-reference electrode and could be suffering from intergranular attack, a precursor for intergranular stress corrosion cracking (IGSCC) in carbon steels [26-28, 30], or other forms of localized corrosion. If the mean potential levels were to stay consistently positive, it could be assumed that the pseudo-reference electrode is corroding preferentially to the working/counter electrode assembly and could be suffering from intergranular or other localized attack. In either case, raw data must be examined before making a corrosion mechanism determination. With the exception of time periods immediately following large water additions, mean potential data indicate that uniform corrosion is the dominant form of corrosion occurring during normal operation of 241-AZ-101. Based on previous laboratory studies, mean potential data also indicate that large water additions to the waste tank temporarily induce localized corrosion in 241-AZ-101 [26-28]. However, raw data from the time periods immediately following water additions must be examined before the exact mechanism of corrosion can be established.

Standard Deviation of Current

A plot of the standard deviation of current over the first two years of operation is shown in Figure 8. Standard deviation of current ranged between approximately 0.1 μA and 0.5 μA over the course of operation. Standard deviation of current levels temporarily reached values of up to approximately 5 μA during large water additions. The average value of the standard deviation of current over the first two years of operation was approximately 0.2 μA.

The trend and behavior of the standard deviation of current noise data were typical of carbon steel electrodes immersed in a high pH, passivating tank waste solution [26-28]. Systems such as these passivate slowly over time. Higher uniform corrosion rates and the onset of localized corrosion typically produce higher levels of the standard deviation of current. As seen in Figure 8, the standard deviation of current is higher immediately following electrode immersion but drops off steadily as the electrodes passivate up to the point of the large water additions made in October 1996. Small values of standard deviation of current are consistent with uniform corrosion at low rates in passive systems. Any major onset of localized corrosion should cause a disruption in the standard deviation data. With the exception of time periods immediately following large water additions, standard deviation of current data indicate that uniform corrosion is the dominant form of corrosion occurring during normal operation of 241-AZ-101. Based on previous laboratory studies and operational history of the 241-AZ-101 system, the standard deviation of current data also indicate that large water additions to the waste tank temporarily induce localized corrosion in 241-AZ-101 [26-28, 30]. However, raw data from the time periods immediately following water additions must be examined before the exact mechanism of corrosion can be established.

Standard Deviation of Potential

A plot of the standard deviation of potential over the first two years of operation is shown in Figure 9. Standard deviation of potential ranged between approximately 0.05 mV and 0.2 mV over the course of operation. Standard deviation of potential levels temporarily reached values of up to approximately 8 mV following large water additions. The average value of the standard deviation of potential over the first two years of operation was approximately 0.1 mV.

The trend and behavior of the standard deviation of potential data were typical of carbon steel electrodes immersed in a high pH, passivating tank waste solution [26-28]. Systems such as these passivate slowly over time. Higher uniform corrosion rates and the onset of localized corrosion typically produce higher levels of the standard deviation of potential. As seen in Figure 9, the standard deviation of potential is higher immediately following electrode immersion but drops off steadily as the electrodes passivate up to the point of the large water additions made in October 1996. Small values of standard deviation of potential are consistent with uniform corrosion at low rates in passive systems. Any major onset of localized corrosion should cause a disruption in the standard deviation data. With the exception of time periods immediately following large water additions, standard deviation of potential data indicate that uniform corrosion is the dominant form of corrosion occurring during normal operation of 241-AZ-101. Based on previous laboratory studies and operational history of the 241-AZ-101 system, the standard deviation of potential data also indicate that large water additions to the waste tank temporarily induce localized corrosion in 241-AZ-101 [26-28, 30]. However, raw data from the time periods immediately following water additions must be examined before the exact mechanism of corrosion can be established.

Pitting Index

The pitting index (PI) parameter has a maximum value of 1.0 and is defined as,

$$PI = \sigma_I/I_{rms} \qquad (1)$$

where σ_I is the standard deviation of current and I_{rms} is the root mean square of current flowing between the counter and working electrodes. High pitting index values are reported to indicate the onset of localized corrosion, whereas lower values indicate uniform corrosion [6-9]. A plot of the pitting index over the first two years of operation is shown in Figure 10. Pitting index values ranged between approximately 0.1 and 1 over the course of operation. Values often temporarily reached 1 following large water additions. The average pitting index level over the first two years of operation was approximately 0.3.

Although high pitting index values are reported to be, and in many instances are, capable of indicating the occurrence of localized corrosion, the value of I_{rms} must be taken into account before broad conclusions can be drawn from pitting index data. Inspection of equation 1 shows that low I_{rms} current values will also drive pitting index values up toward 1.0. Thus, as with other statistical data, raw data must be examined and correlated with pitting index data to get a true feel for what is going on in the system being observed.

With the exception of time periods immediately following large water additions, pitting index data indicate that uniform corrosion is the dominant form of corrosion occurring during normal operation of 241-AZ-101. Based on previous laboratory studies and operational history of the 241-AZ-101 system, pitting index data also indicate that large water additions to the waste tank temporarily induce localized corrosion in 241-AZ-101 [26-28, 30]. However, raw data from the time periods immediately following water additions must be examined before the exact mechanism of corrosion can be established.

Resistance Noise

The resistance noise (R_n) for a system is defined as,

$$R_n = \sigma_{EPN}/\sigma_{ECN} \tag{2}$$

where σ_{EPN} is the standard deviation of potential and σ_{ECN} is the standard deviation of current. The trend in R_n over the first two years of operation is shown in Figure 11. Resistance noise levels ranged between approximately 200 Ω and 2000 Ω over the course of operation. Resistance noise levels temporarily reached values of over 12 kΩ following some large water additions. The average of resistance noise data over the first two years of operation was approximately 700 Ω.

The trend and behavior of the resistance noise data were typical of carbon steel electrodes immersed in a high pH, passivating tank waste solution [26-28]. Systems such as these passivate slowly over time. Higher uniform corrosion rates and the onset of localized corrosion typically produce higher levels of resistance noise. As seen in Figure 11, the resistance noise level is higher immediately following electrode immersion but drops off steadily as the electrodes passivate up to the point of the large water additions made in October 1996. Small values of resistance noise are consistent with uniform corrosion at low rates in passive systems. Any major onset of localized corrosion should cause a disruption in the resistance noise data. With the exception of time periods immediately following large water additions, resistance noise data indicate that uniform corrosion is the dominant form of corrosion occurring during normal operation of 241-AZ-101. Based on previous laboratory studies and operational history of the 241-AZ-101 system, the resistance noise data also indicate that large water additions to the waste tank temporarily induce localized corrosion in 241-AZ-101 [26-28, 30]. However, raw data from the time periods immediately following water additions must be examined before the exact mechanism of corrosion can be established.

R_n Based Uniform Corrosion Rates

Although it is highly unlikely that waste tanks at Hanford will ever fail from uniform corrosion, uniform corrosion rate information is currently demanded by site operating guidelines and for guidance when adjusting waste alkalinity and other chemical concentration variables [1,2]. At Hanford, uniform corrosion rates are currently estimated based on the comparison of tank waste chemistry sampling data to a series of extensive laboratory weight loss/mechanism studies that exposed tank steels to a variety of possible simulated waste composition [3].

In other industries, uniform corrosion rates have traditionally been calculated from weight loss measurements on coupons or by using standardized Tafel or LPR electrochemical techniques. The expense, contamination and radiation exposure issues associated with gathering weight loss data from coupons exposed to highly radioactive waste tank environments almost completely reduce the viability of this technique in this day and age. Although most of the contamination and radiation exposure issues can be avoided by using Tafel and LPR techniques, both of these techniques are disruptive, to various degrees, to the electrode surfaces. More simply put, the surface to be studied is changed, at least temporarily, by the method of study. Although the primary advantage of using EN to study corrosion is the technique's ability to detect and discriminate between forms of localized corrosion, the advantages to also being able to passively, safely, and economically collect uniform corrosion rate data are inherently obvious.

It has been proposed that values of R_n calculated from EN data can be used in place of polarization resistance (R_p) in conjunction with the Stern-Geary constant and Faraday's second law to calculate uniform corrosion rates [6, 8, 31]. However, when computing corrosion rates from R_n data collected on a standard three electrode EN probe, the value of R_n must be modified to account for surface area of the electrodes and the fact that the potential noise signal is being collected from two electrodes rather than one. Equation 3 shows R_n for use in uniform corrosion rate calculations,

$$R_n = (\sigma_{EPN} / \sigma_{ECN})(A/\sqrt{2}) \tag{3}$$

where σ_{EPN} is the standard deviation of potential, σ_{ECN} is the standard deviation of current, and A is the surface area of one electrode. Uniform corrosion rate data estimated from R_n is shown in Figure 12. Corrosion rates ranged between approximately 0.1 mil per year (mpy) to 2 mpy over the course of normal operation. The uniform corrosion rate calculated from resistance noise was approximately 0.7 mpy over the first two years of operation.

Corrosion rates temporarily reached values of over 5 mpy following some large water additions. However, historical data and laboratory studies indicate that pit initiation is often induced by large water additions to 241-AZ-101 [26-28, 30]. Therefore, raw data must be examined before accepting uniform corrosion data calculated from R_n. Time periods in which raw data reveal pitting or other localized corrosion must be ignored when calculating *uniform* corrosion rate information from R_n or other techniques. Uniform corrosion rates measured on electrodes undergoing pitting or other forms of localized corrosion will be falsely inflated by the high current densities associated with localized attack.

R_p Based Uniform Corrosion Rates

In an effort to validate corrosion rates generated from resistance noise data a series of Tafel and LPR tests were run in between August and September 1996 and again in September 1998. The effects of Tafel tests conducted in September 1996 are obvious in some of the statistical data plots as short-lived positive spikes. Average Tafel slopes calculated from these tests were $b_c = 46$ mV/decade and $b_a = 214$ mV/decade. In the eight LPR tests, the measured value of R_p was approximately four times greater than the value of R_n measured shortly before the onset of LPR testing. This difference could be related to a lack of potential sensitivity in the instrumentation or signal loss through the long data cable. Although different by a factor of four, R_p appears to track R_n in the 241-AZ-101 system. Corrosion rates calculated from R_p data are four times lower than rates calculated from R_n data as shown in Figure 13.

SUPERNATE RAW DATA - OFF NORMAL CONDITIONS

As shown in Table 1, eight separate major water additions of over 6,500 gal (24,600 L) were made to tank 241-AZ-101 over the first two-years of operation. Of these, the additions made on 10/3/96, 10/24/96, 12/18/96, 1/16/97, 2/12/97, 4/28/97, 8/16/97, and 11/25/97 strongly affected the corrosion behavior of the tank. With the exception of the 12/18/96 addition, raw data files from the time periods surrounding these water additions were closely investigated. Equipment suffered a loss of power shortly before the 12/18/96 addition and no data related to the event were recorded. Raw data prior to water additions in all cases is typical of uniform corrosion in passive systems. With the exception of the 8/16/97 water addition, which was performed more slowly, raw data from after each large water addition is typical of pit initiation and growth. No pit initiation or growth was recorded following the 8/16/97 addition. Data indicative of pit initiation and growth following large water additions to tank 241-AZ-101 at the Hanford site are consistent with previously published predictions of pitting behavior in waste tanks at other nuclear waste storage facilities [32].

It is immediately obvious from inspection of the potential data presented in Figures 14 - 27 that the potential measurement instrumentation in the 241-AZ-101 EN equipment is not sensitive enough to record the minute potential fluctuations associated with pitting in very passive systems. Potential measurement sensitivity would have to be improved by several orders of magnitude to be capable of accurately measuring pitting transients in the waste tank. However, current data is exceptionally good.

Raw data files are presented in chronological order based on the start time of the water addition. Raw current and potential data from shortly before and shortly after the 26,646 L addition made on 10/3/96 are shown in Figures 14 and 15 respectively. Raw current and potential data from shortly before and shortly after the 88,162 L addition made on 10/24/96 are shown in Figures 16 and 17 respectively. Raw current and potential data from shortly before and shortly after the 24,773 L addition made on 1/16/97 are shown in Figures 18 and 19 respectively. Raw current and potential data from shortly before and shortly after the 90,556 L addition made on 2/12/97 are shown in Figures 20 and 21 respectively. Raw current and potential data from shortly before and shortly after the 98,883 L addition made on 4/28/97 are shown in Figures 22 and 23 respectively. Raw current and potential data from shortly before and shortly after the 88,474 L addition made between 8/16/97 and 8/22/97 are shown in Figures 24 and 25 respectively. Raw current and potential data from shortly before and shortly after the 100,549 L addition made on 11/25/97 are shown in Figures 26 and 27 respectively.

SUPERNATE RAW DATA - NORMAL OPERATIONAL CONDITIONS

One of the greatest potential problems with the use of EN as a corrosion monitoring technique is the large volume of raw data produced. Since over 50,000 raw data files with 600 points of data per file have been collected to date on the 241-AZ-101 corrosion monitoring system, it is not practical or necessary to present all the raw data. However, it is possible to present representative data from each month of operation. Prior to the selection of the files for presentation, many raw data files were analyzed. Up until the last few months of operation, only raw data files collected after large water additions presented any substantial indication of localized corrosion, and in all cases the mechanism has been temporary pit initiation and some growth. With the exception of March, July and August 1998, most other files are typical of uniform corrosion. Data collected from March, July and August 1998 display a cyclic pattern in current that has not yet been fully analyzed. Further analysis and comparison with tank farm operational records will be necessary before a full determination can be made on the source of the cyclic pattern in the data. However, discussions with other parties have indicated that crevice corrosion may be responsible for the cyclic current behavior.

Raw current and raw potential data files typical of each month of operation are presented in chronological order in Figures 28 - 50. Raw data are presented in sets of two plots per figure, a plot of current versus time followed by a plot of potential versus time. Time scales are the same on all plots. Each plot displays 600 points collected at one second intervals. Plots are full scaled for maximum detail in each case. Data were collected from each month since the probe installation with the exception of December 1997 and January 1998 when an unknown party disconnected the instrument from its power supply. Based on this analysis, uniform corrosion is most likely the dominant mode of corrosion occurring in tank 241-AN-107. Figure 28 shows raw current and potential from August 1996. Figure 29 shows raw current and potential from September 1996. Figure 30 shows raw current and potential from October 1996. Figure 31 shows raw current and potential from November 1996. Figure 32 shows raw current and potential from December 1996. Figure 33 shows raw current and potential from January 1997. Figure 34 shows raw current and potential from February 1997. Figure 35 shows raw current and potential from March 1997. Figure 36 shows raw current and potential from April 1997. Figure 37 shows raw current and potential from May 1997. Figure 38 shows raw current and potential from June 1997. Figure 39 shows raw current and potential from July 1997. Figure 40 shows raw current and potential from August 1997. Figure 41 shows raw current and potential from September 1997. Figure 42 shows raw current and potential from October 1997. Figure 43 shows raw current and potential from November 1997. Figure 44 shows raw current and potential from February 1998. Figure 45 shows raw current and potential from March 1998. Figure 46 shows raw current and potential from April 1998. Figure 47 shows raw current and potential from May 1998. Figure 48 shows raw current and potential from June 1998. Figure 49 shows raw current and potential from July 1998. Figure 50 shows raw current and potential from August 1998.

CONCLUSIONS AND OBSERVATIONS

- A prototype corrosion-monitoring instrument was installed into tank 241-AZ-101 at the Hanford Site in August 1996. The instrument monitors transients in corrosion current and corrosion potential occurring on electrodes immersed in the waste liquid and suspended in the vapor space above the waste. By monitoring these transients, changes in the corrosive characteristics of the waste have been rapidly detected and correlated with operational changes in the tank.
- Condensate and flush water additions made on 10/3/96, 10/24/96, 12/18/96, 1/16/97, 2/12/97, 4/28/97, 8/16/97, and 11/25/97 strongly affected the corrosion behavior of the tank. Each of these water additions was over 6,500 gal (24,600 L) in volume. Raw data prior to water additions in all cases is typical of uniform corrosion in passive systems. Raw data collected after each large water addition is typical of pit initiation and growth. Pitting transients persisted for a few weeks after the water additions in each case.
- Reducing the delivery rate of the water additions to the tank would likely reduce the tendency to induce pit initiation and growth.
- Data collected during normal operation of the tank (not following water additions) indicate that uniform corrosion is the dominant corrosion mechanism in 241-AZ-101.
- Data indicative of pit initiation and growth following large water additions to tank 241-AZ-101 at the Hanford site are consistent with previously published predictions of pitting behavior in waste tanks at other nuclear waste storage facilities.

- The potential measurement systems of the 241-AZ-101 EN equipment are not sensitive enough to record the minute potential fluctuations associated with pitting in tank 241-AZ-101. Potential measurement sensitivity would have to be improved by several orders of magnitude to be capable of accurately measuring pitting transients in the waste tank. However, current data is exceptionally good.
- Values of R_p measured by LPR were approximately 4 times greater than the R_n values calculated from the EN data. Tafel constants (determined by Tafel extrapolation) were $b_c = 46$ and $b_a = 214$ mV/decade. During uniform corrosion (verified by inspection of raw EN data), corrosion rates determined from both LPR measurements and EN data were less than 1 mpy.
- Data collected from the Hanford Site prototype corrosion probe indicates that an EN/LPR based corrosion monitoring system can be successfully applied to nuclear waste tank environments.

ACKNOWLEDGMENTS

This work represents the cooperative efforts of many people and organizations from extremely diverse backgrounds and ranges of interest. Without the collaborative efforts of these individuals, there would still be no corrosion monitoring at the Hanford Site. The laboratory tests leading to the development of this system were conducted over the course of two years by personnel from the Materials and Corrosion Engineering group within Lockheed Martin Hanford Corporation, the Corrosion Science and Technology Group at Oak Ridge National Laboratory, and the Materials Development group of the Structural Materials Research Section at Pacific Northwest National Laboratory. The technical support of Mr. J. L. Nelson of Lockheed Martin Hanford Corporation, Dr. G. E. C. Bell of M. J. Schiff & Associates, Dr. K. E. Lawson of The Mentor_1 Group, Dr. A. N. Rothwell of C^3 Ltd., is also gratefully acknowledged.

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TABLES

TABLE 1: WATER ADDITIONS TO 241-AZ-101

Water Addition	**Date**	**Volume (gal)**	**Volume (L)**	**Source**
1	October 3, 1996	7,040	26,646	Transfer from 152-AX including 500 gallons treated with 10-15% NaOH
2	October 23, 1996	23,293	88,162	Condensate water from 417-A
3	December 18, 1996	24,145	91,389	Condensate water from 417-A
4	January 16, 1997	6,545	24,773	Transfer from 151-AZ
5	February 12, 1997	23,925	90,556	Condensate water from 417-A
6	April 28, 1997	26,125	98,883	Condensate water from 417-A
7	August 16-22, 1997	23,375	88,474	Condensate water from 417-A
8	November 25, 1998	26,565	100,549	Condensate water from 417-A

FIGURES

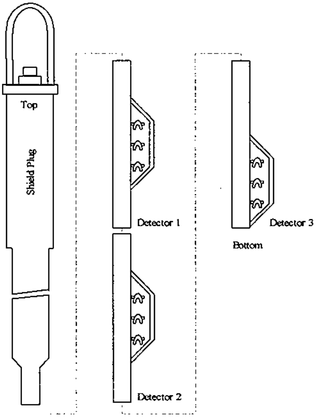


Figure 1: Schematic of 241-AZ-101 corrosion probe body

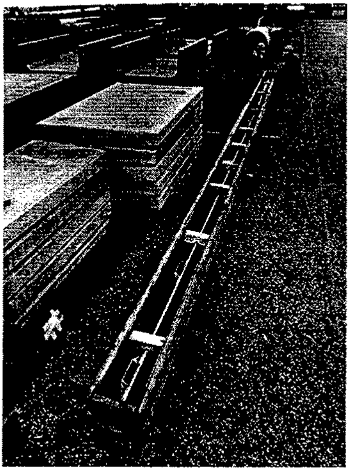


Figure 2: Probe body in shipping container prior to installation into 241-AZ-101

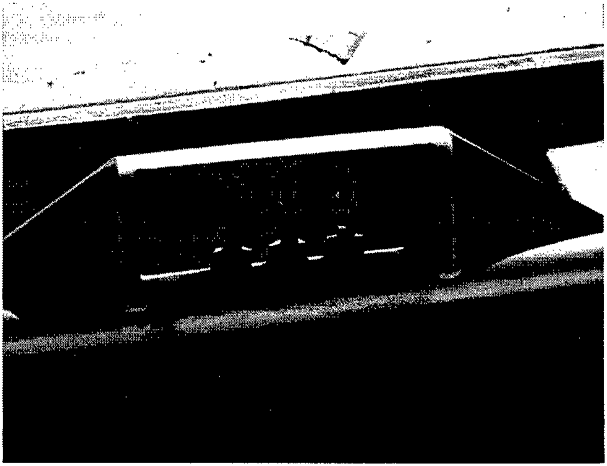


Figure 3: Detail of 241-AZ-101 corrosion probe electrode array

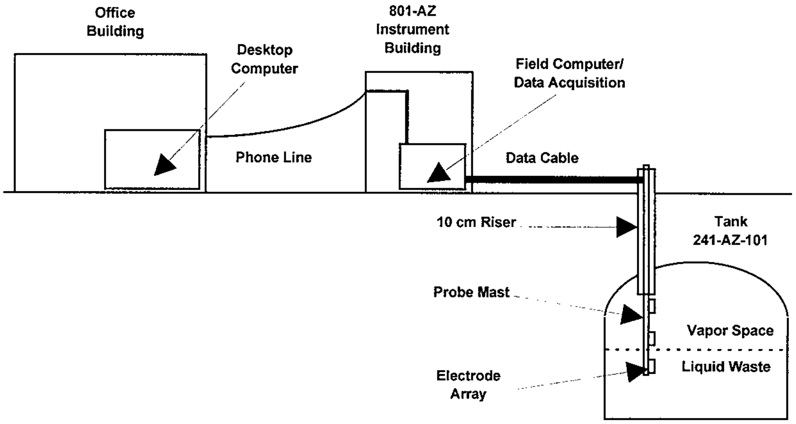


Figure 4: 241-AZ-101 corrosion monitoring system schematic

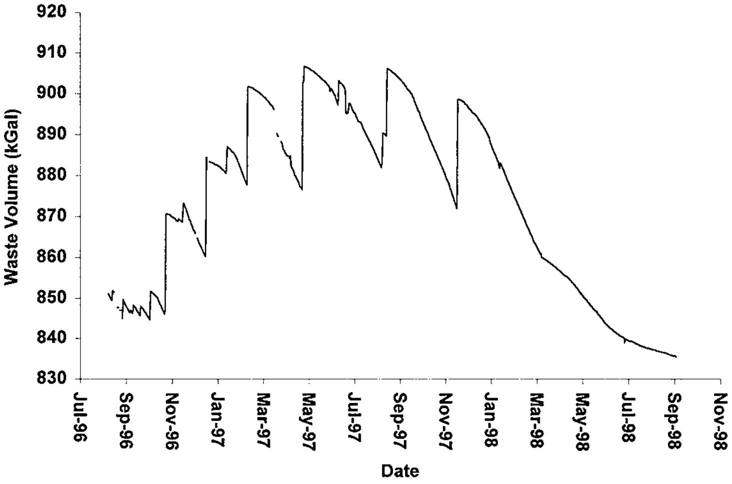


Figure 5: Tank 241-AZ-101 waste volume

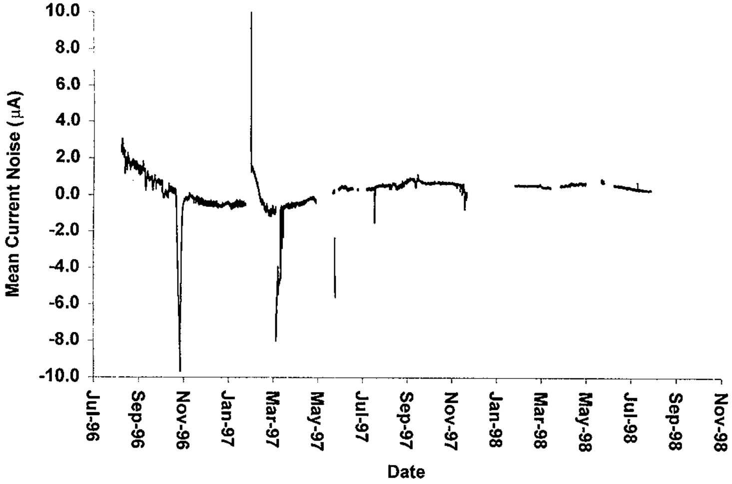


Figure 6: Mean current noise

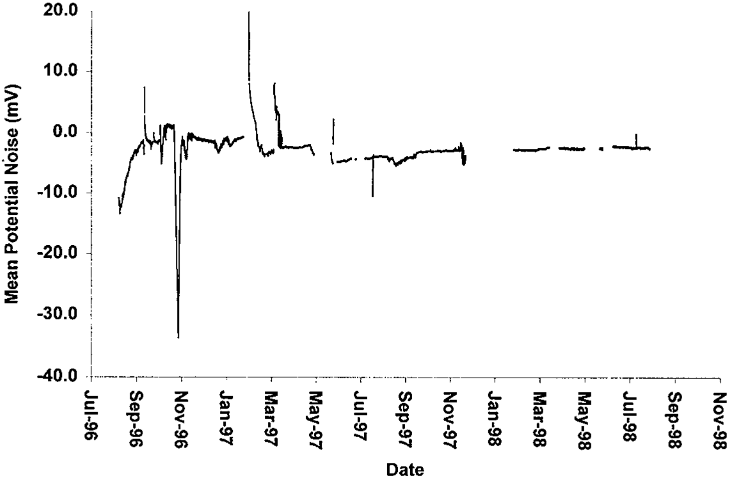


Figure 7: Mean potential noise

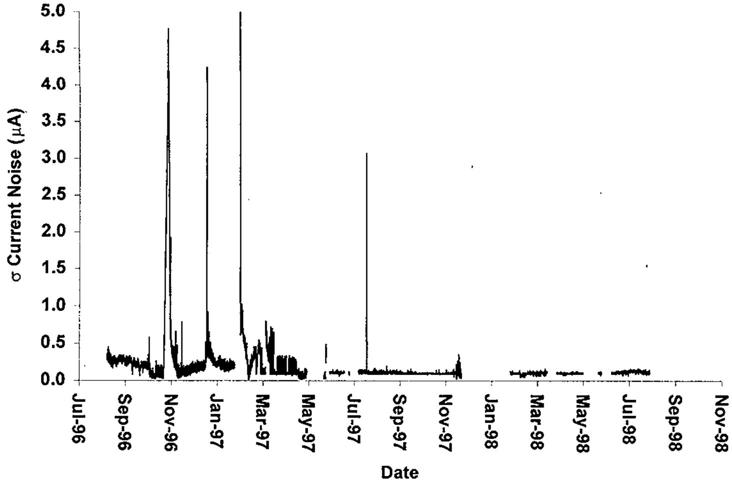


Figure 8: Standard deviation of current noise

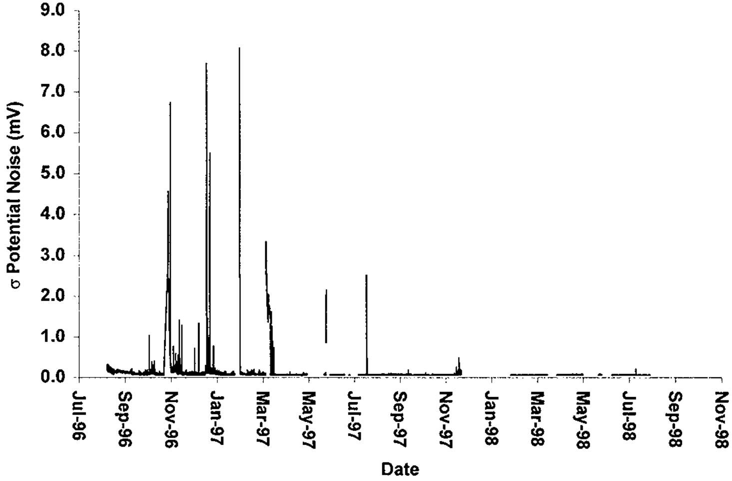


Figure 9: Standard deviation of potential noise

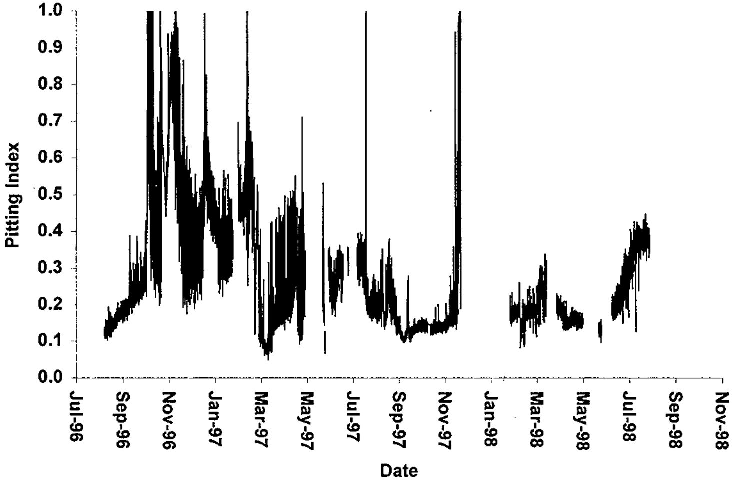


Figure 10: Pitting index

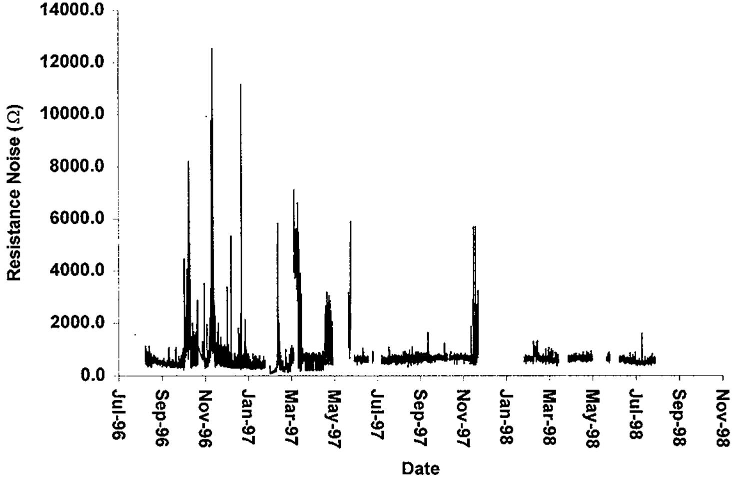


Figure 11: Resistance noise

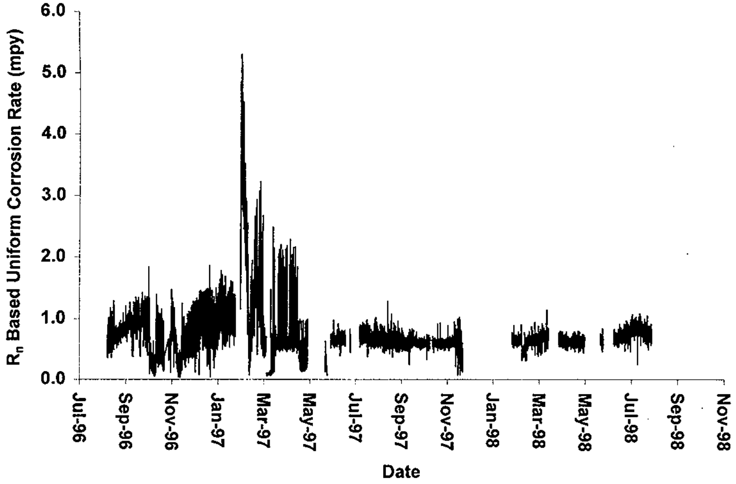


Figure 12: Uniform corrosion rate from R_n data

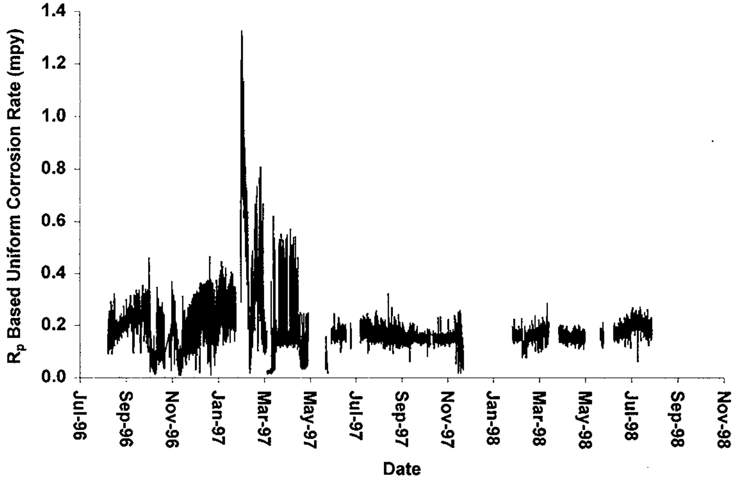


Figure 13: Uniform corrosion rate from R_p data

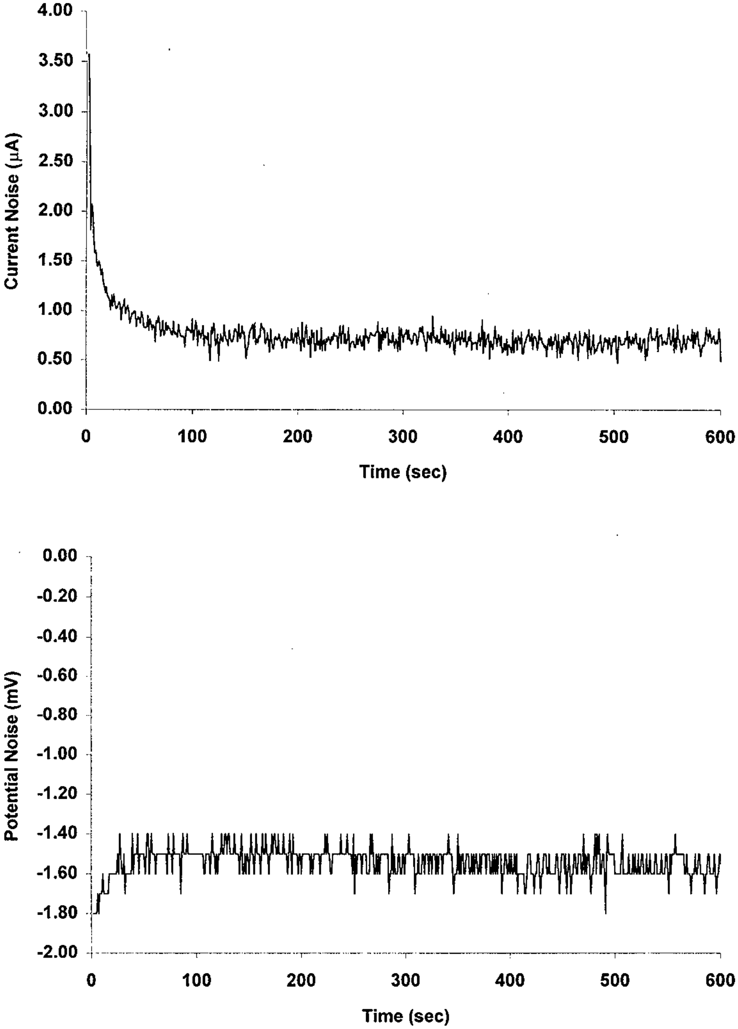
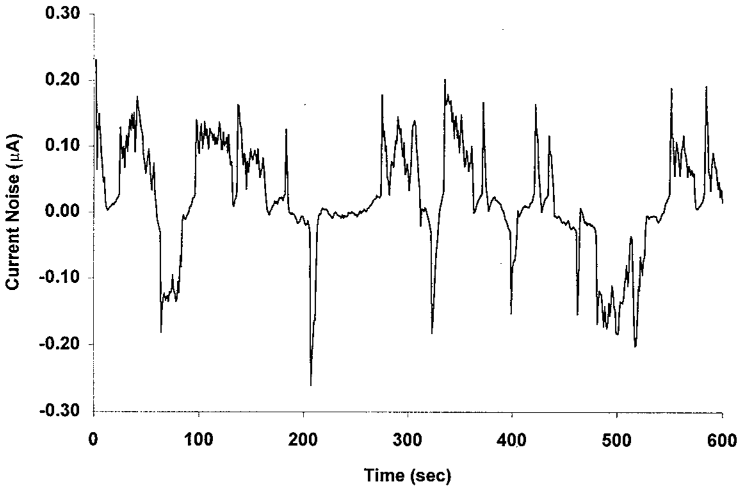


Figure 14: Raw current and potential data collected prior to the 26,646 L addition made on 10/3/96



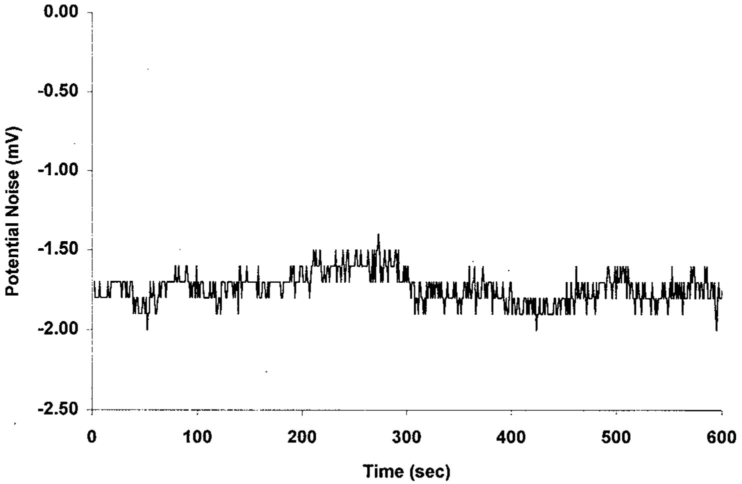


Figure 15: Raw current and potential data collected after the 26,646 L addition made on 10/3/96

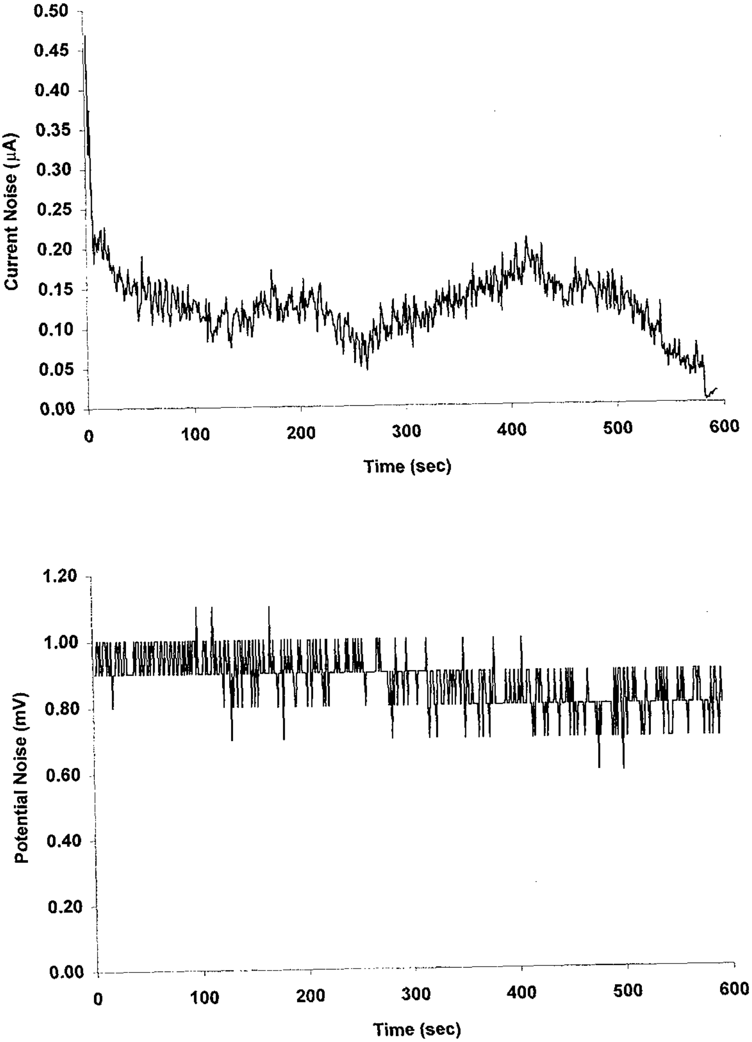
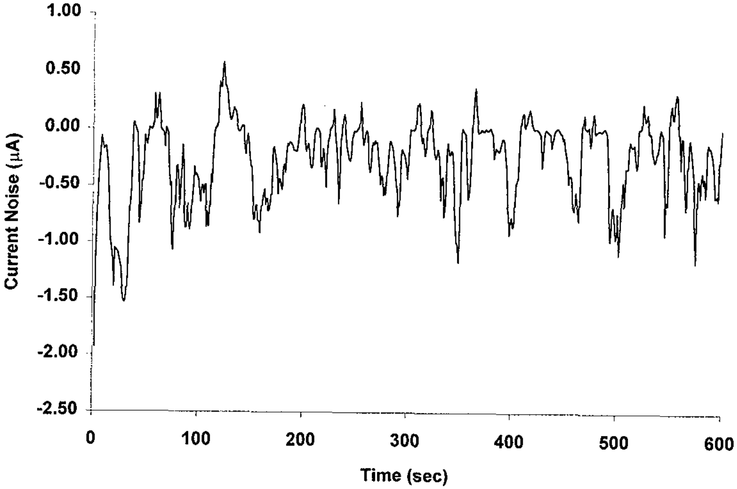


Figure 16: Raw current and potential data collected prior to the 88,162 L addition made on 10/24/96



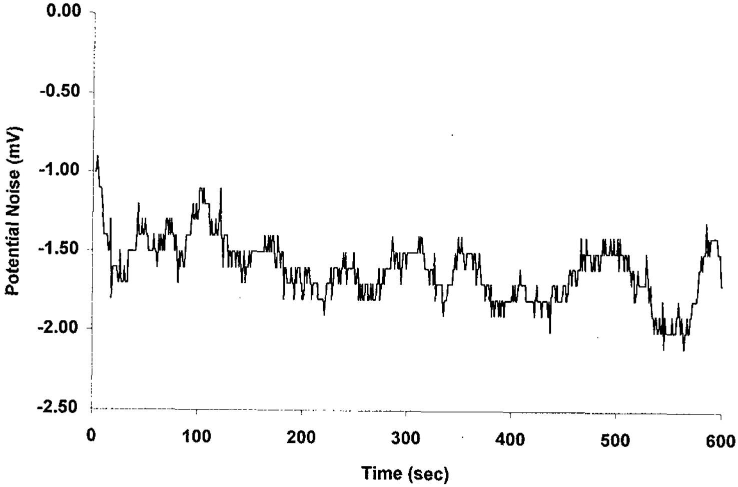


Figure 17: Raw current and potential data collected after the 88,162 L addition made on 10/24/96

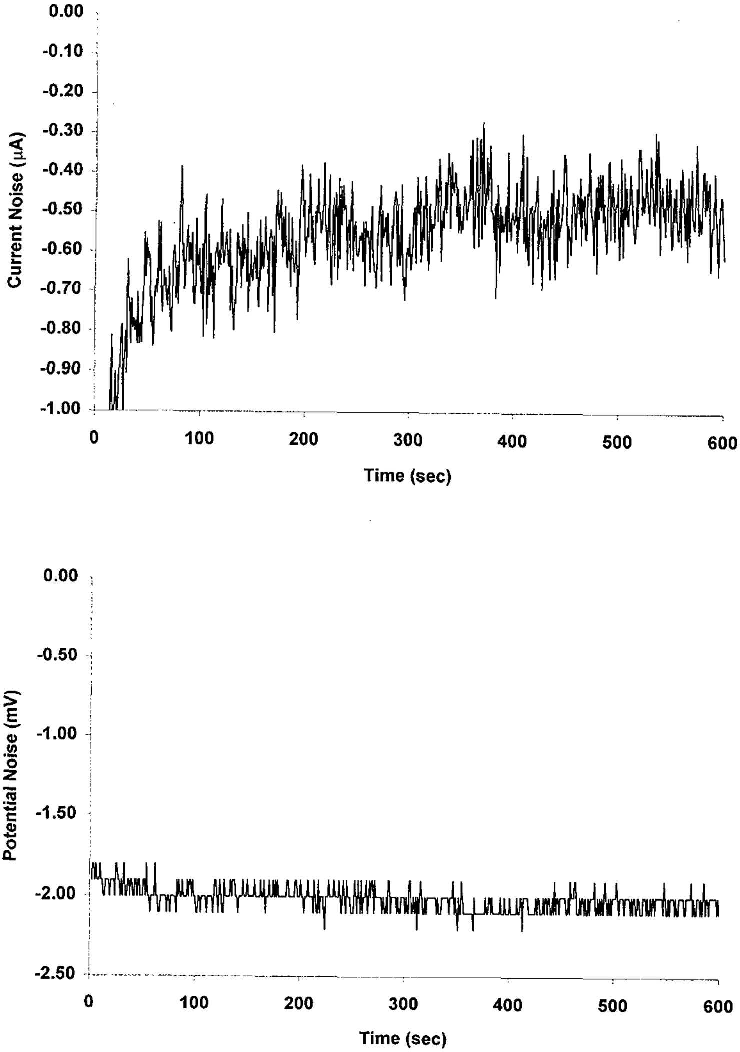
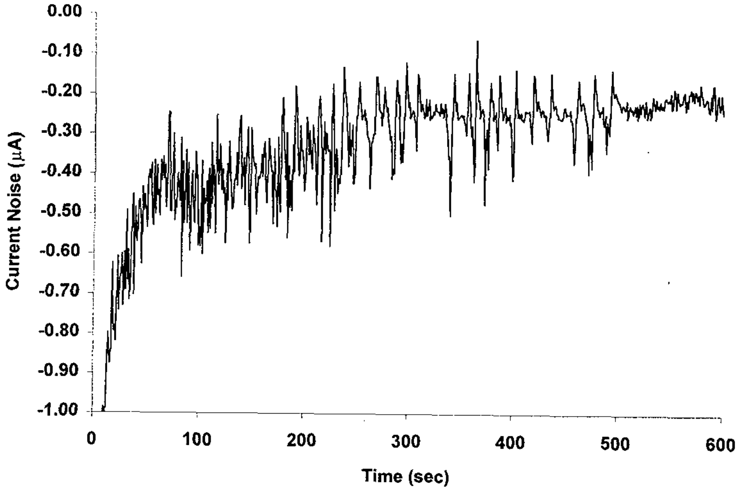


Figure 18: Raw current and potential data collected prior to the 24,773 L addition made on 1/16/97



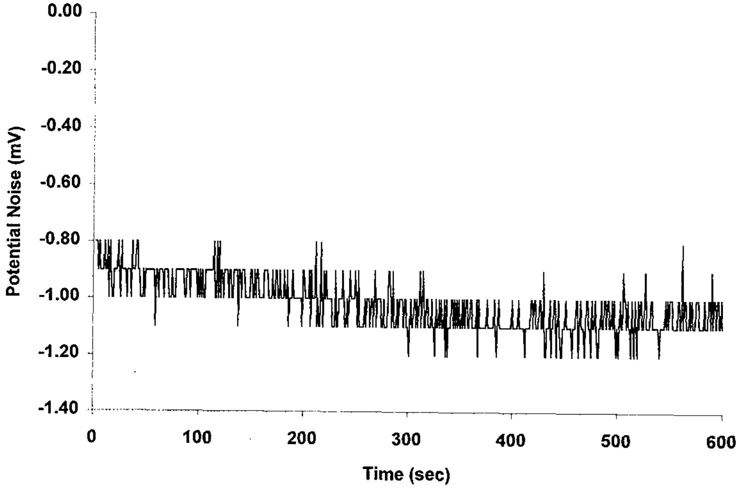


Figure 19: Raw current and potential data collected after the 24,773 L addition made on 1/16/97

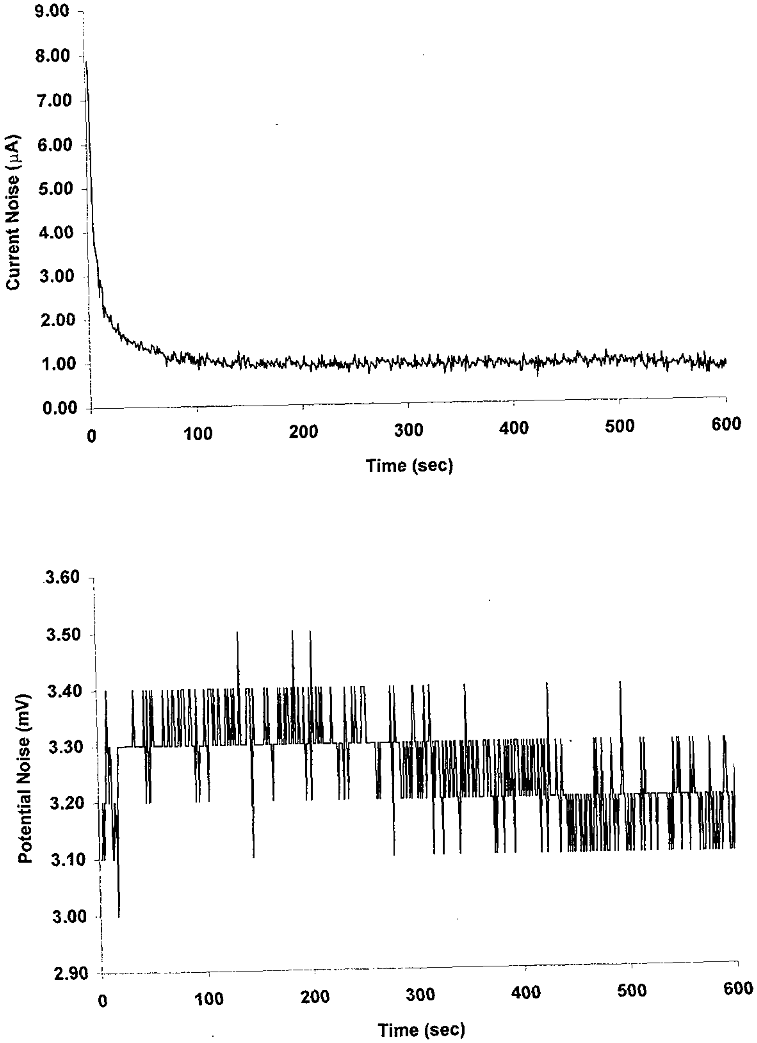


Figure 20: Raw current and potential data collected prior to the 90,556 L addition made on 2/12/97

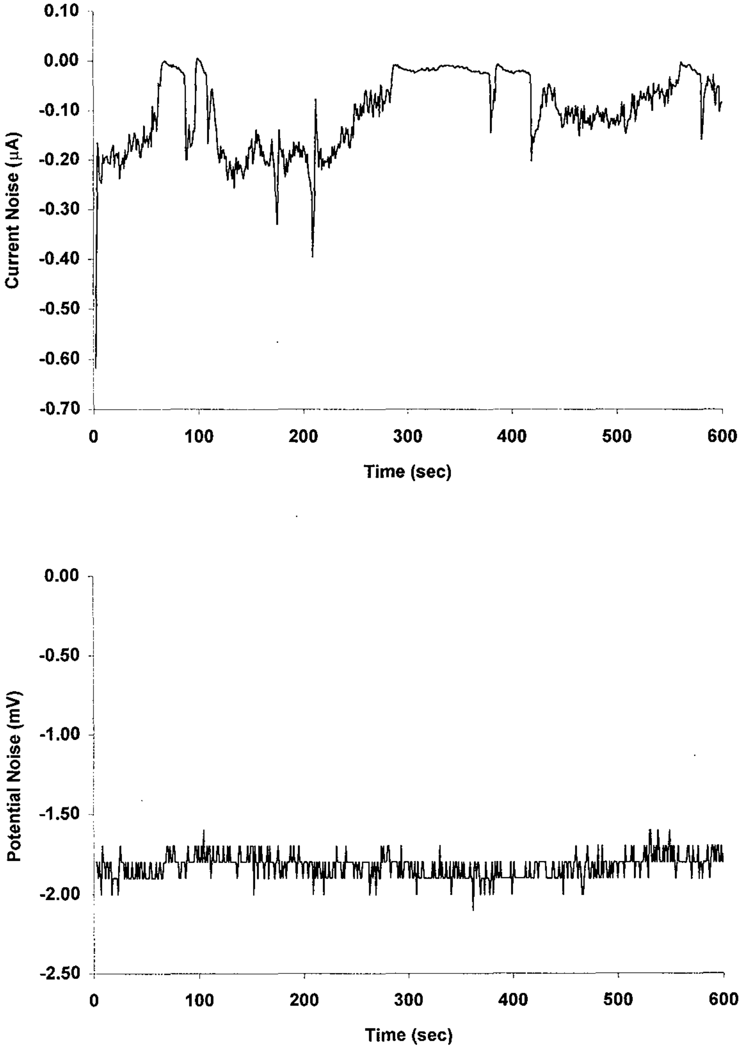


Figure 21: Raw current and potential data collected after the 90,556 L addition made on 2/12/97

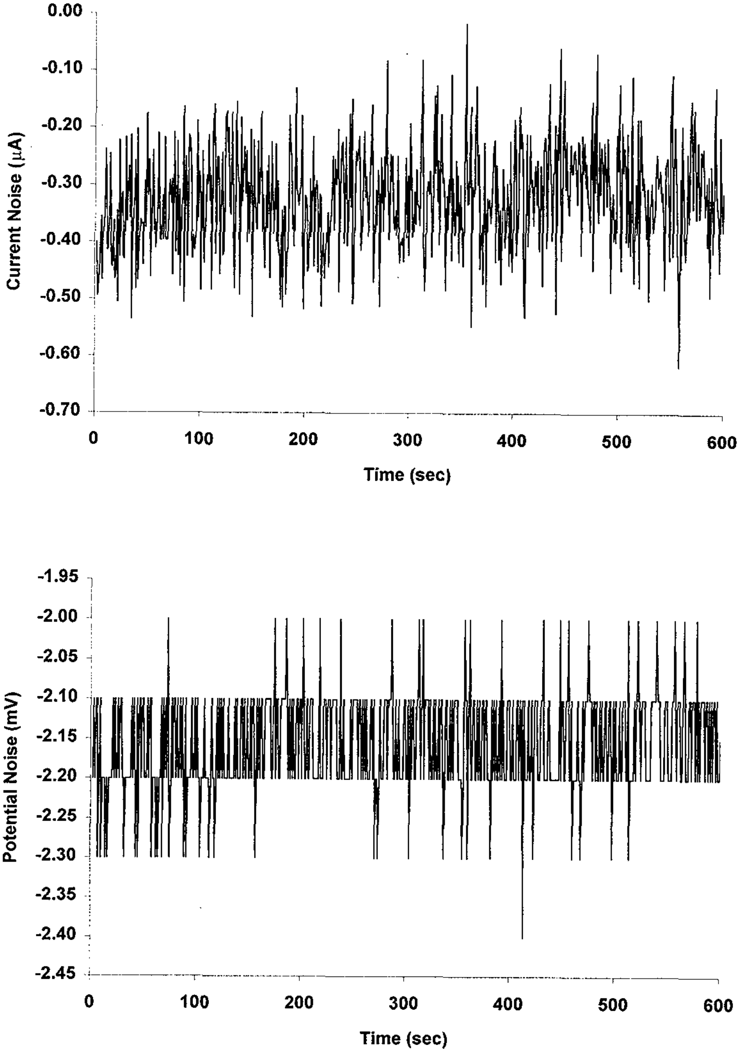
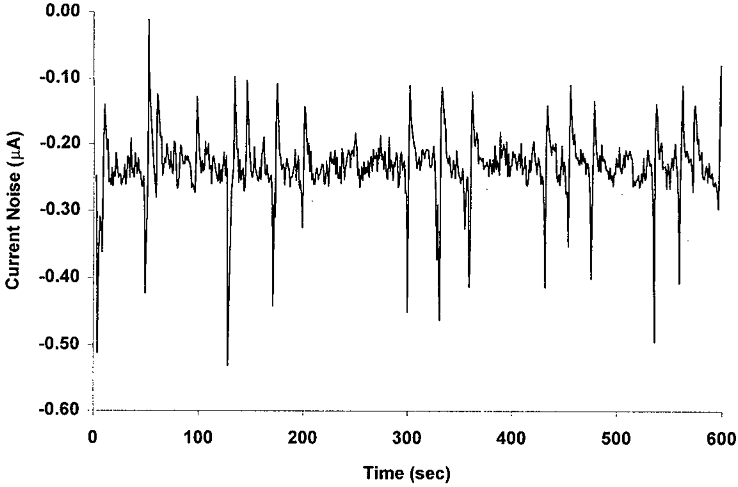


Figure 22: Raw current and potential data collected prior to the 98,883 L addition made on 4/28/97



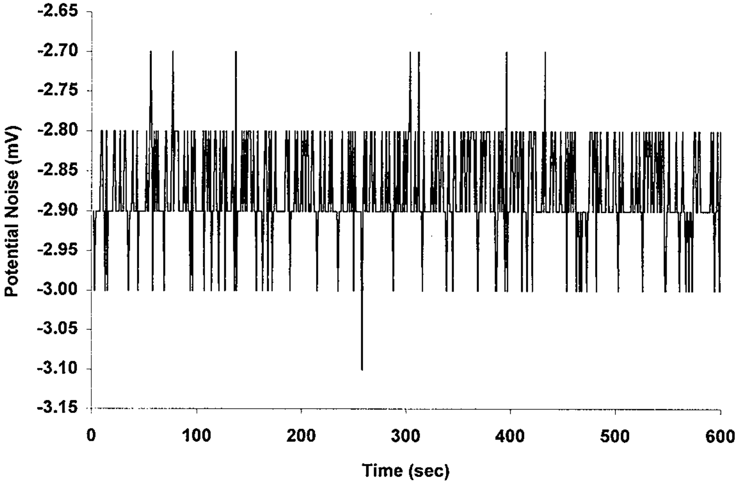


Figure 23: Raw current and potential data collected after the 98,883 L addition made on 4/28/97

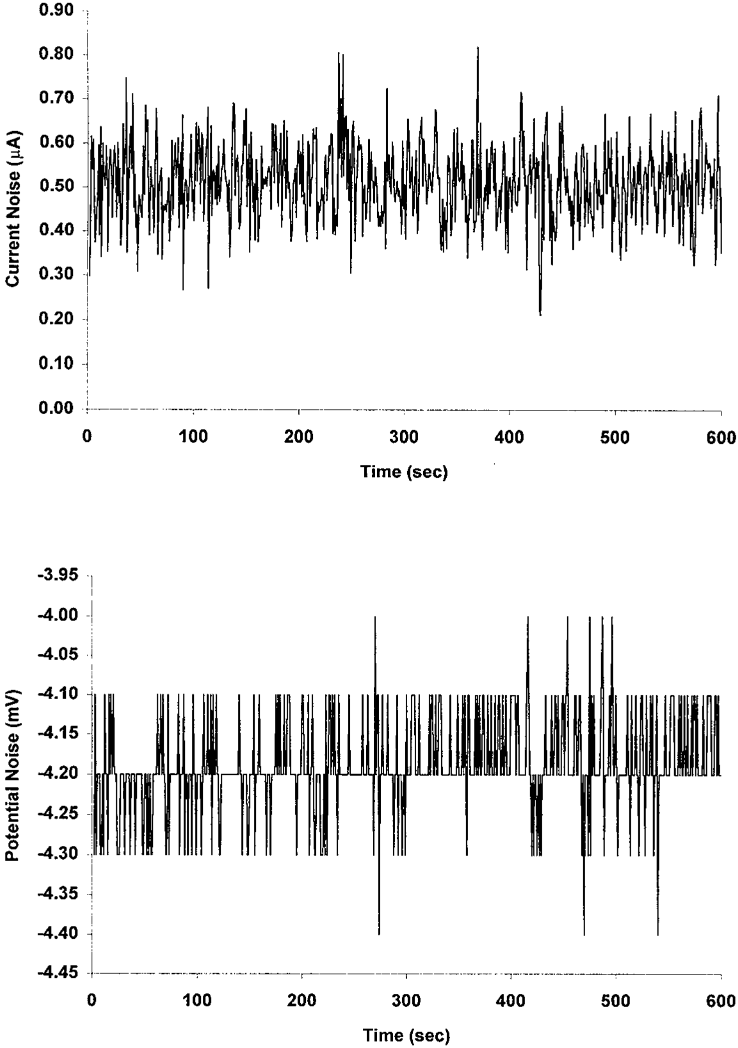


Figure 24: Raw current and potential data collected prior to the 88,474 L addition made between 8/16/97 and 8/22/97

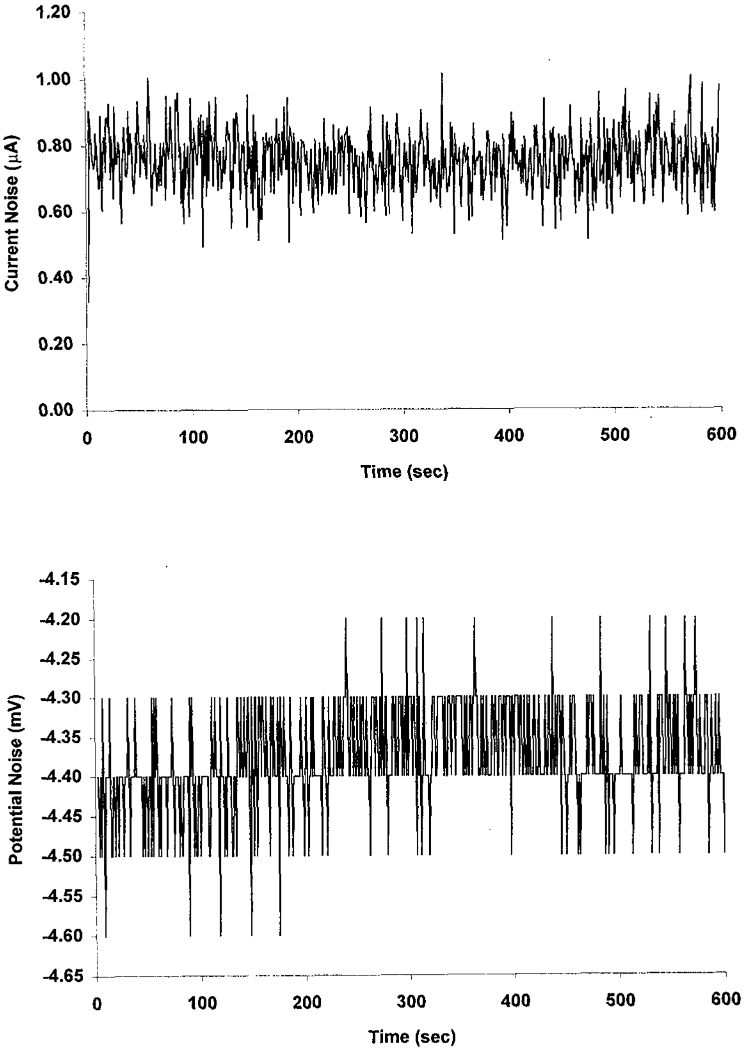


Figure 25: Raw current and potential data collected after the 88,474 L addition made between 8/16/97 and 8/22/97

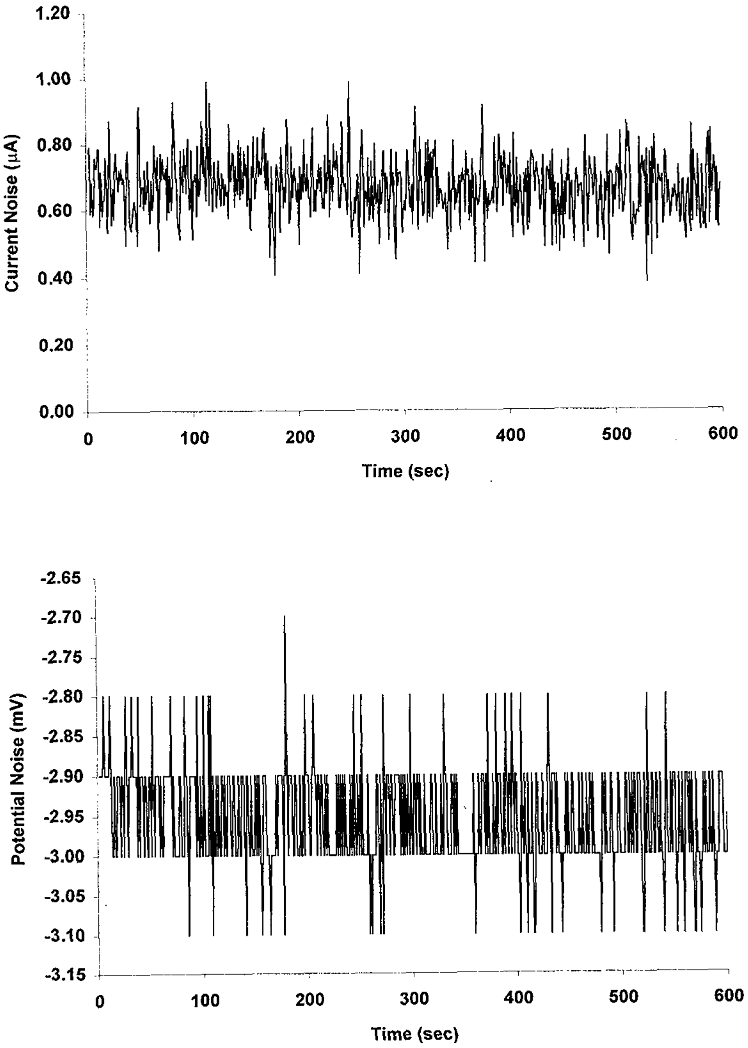
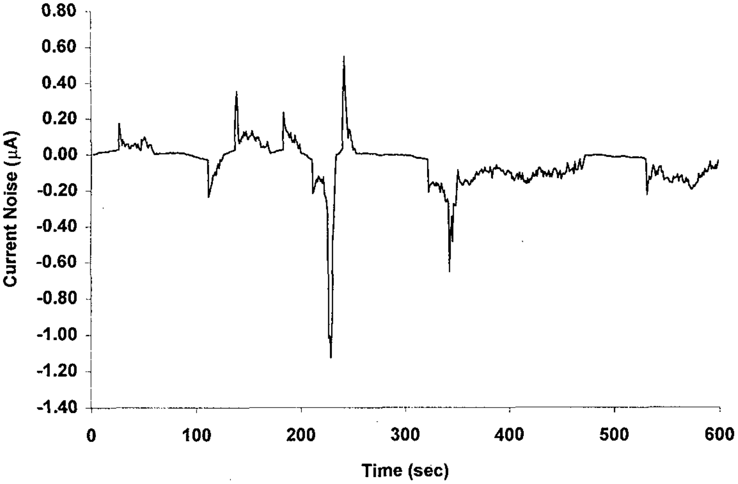


Figure 26: Raw current and potential data collected prior to the 100,549 L addition made on 11/25/97



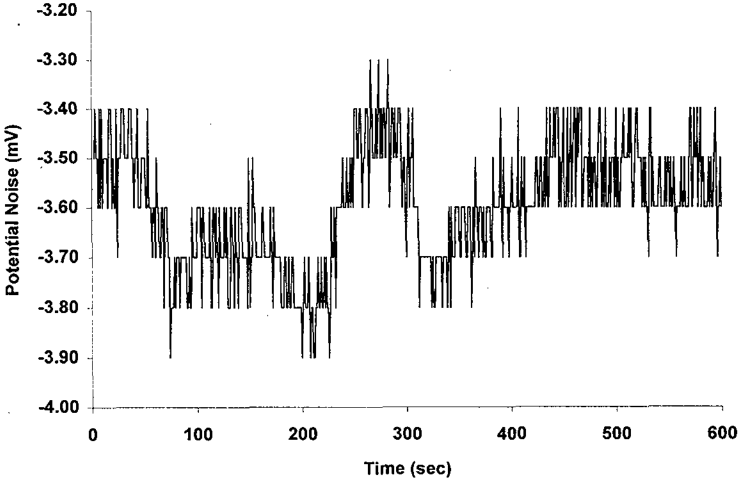


Figure 27: Raw current and potential data collected after the 100,549 L addition made on 11/25/97

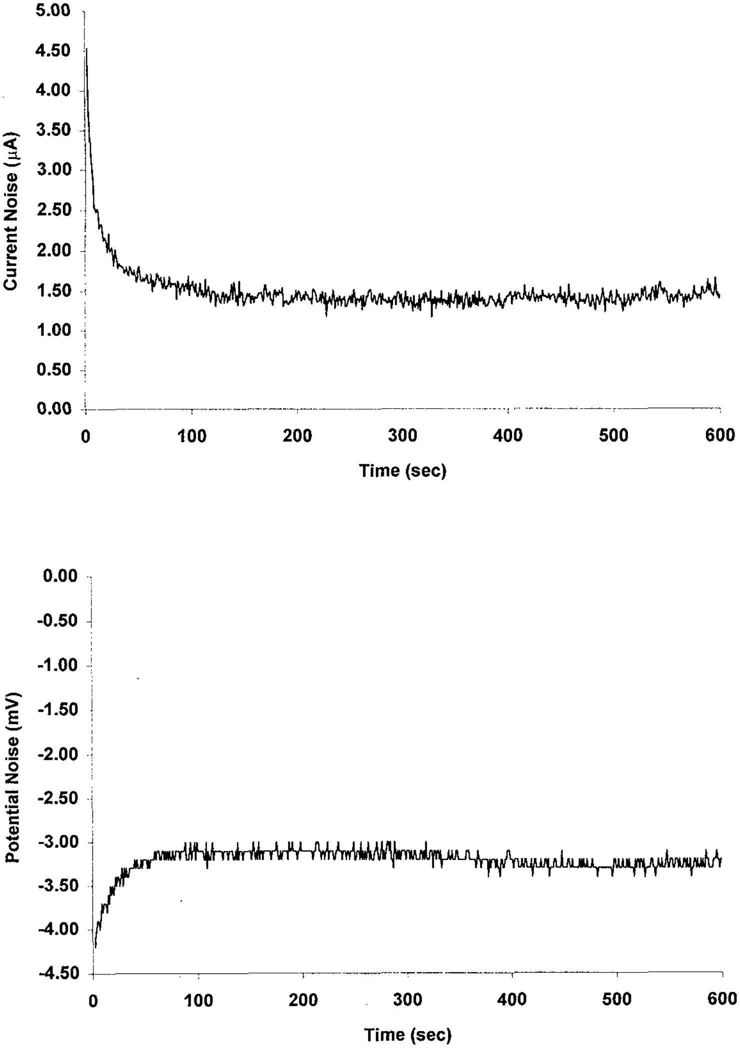


Figure 28: Raw current and potential from August 1996

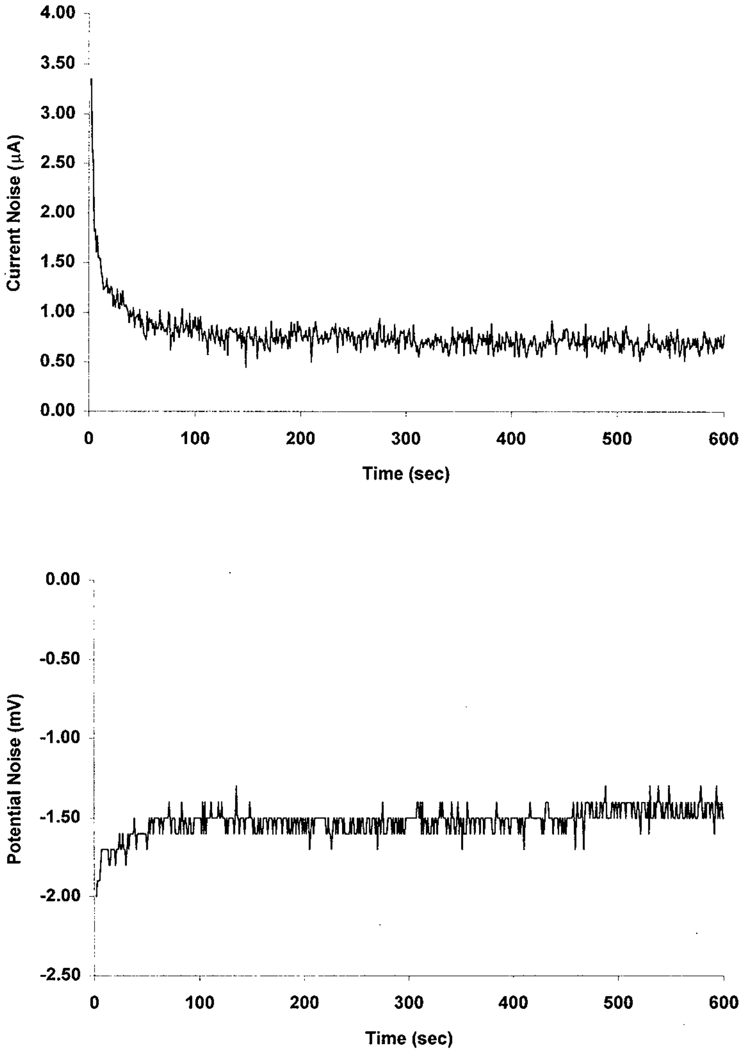


Figure 29: Raw current and potential from September 1996

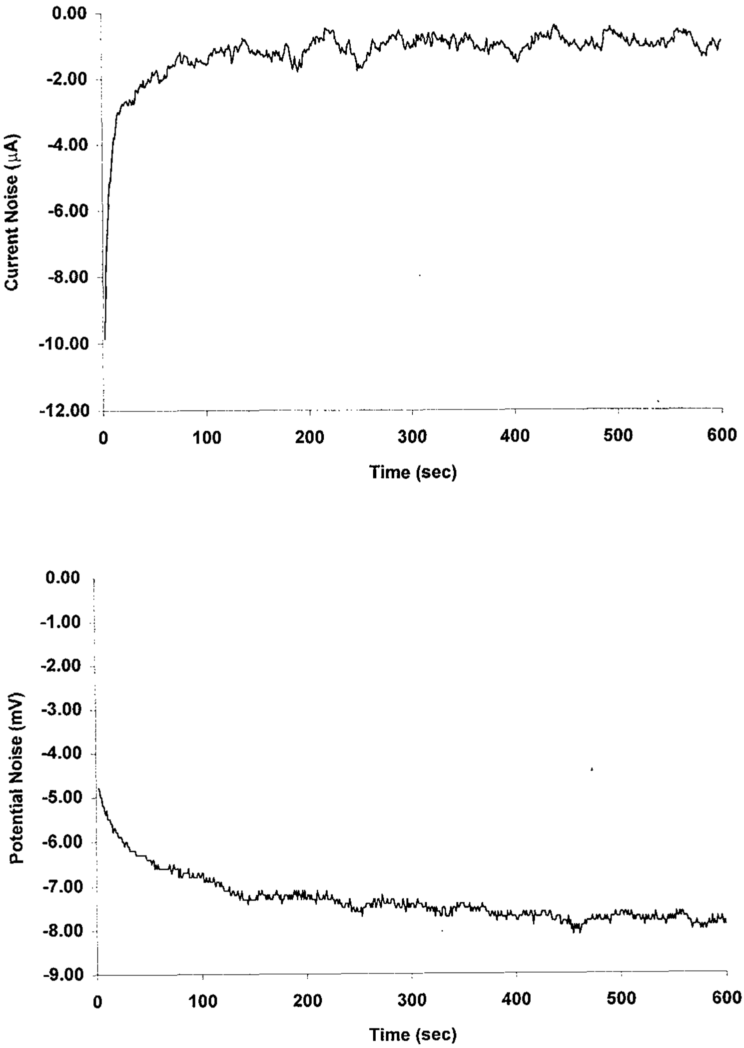
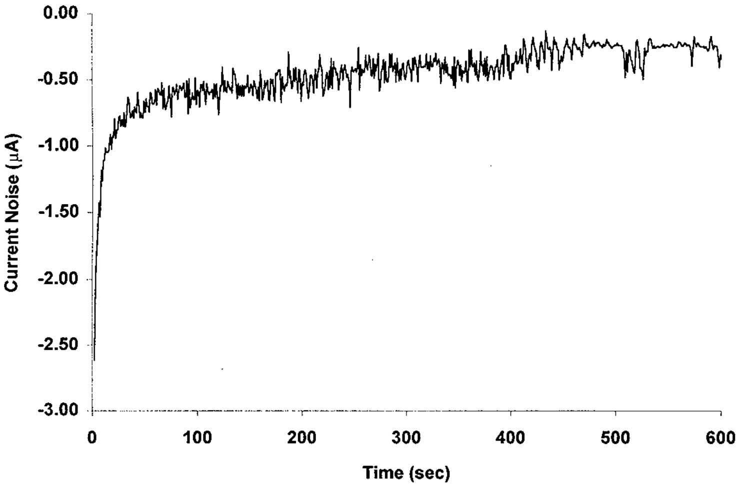


Figure 30: Raw current and potential from October 1996



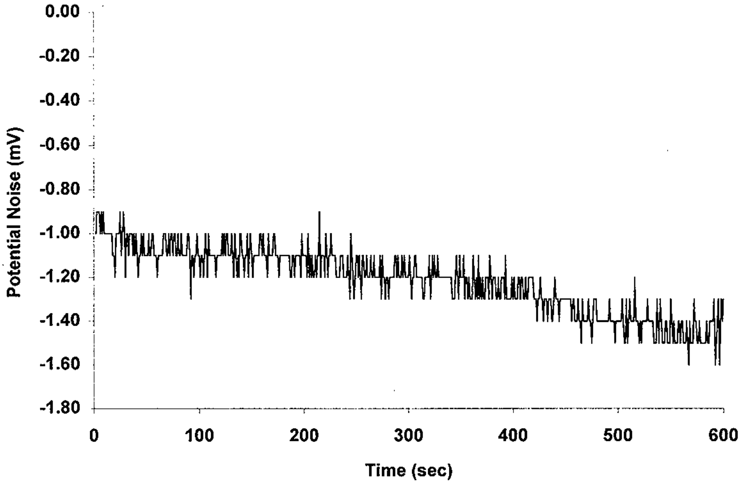


Figure 31: Raw current and potential from November 1996

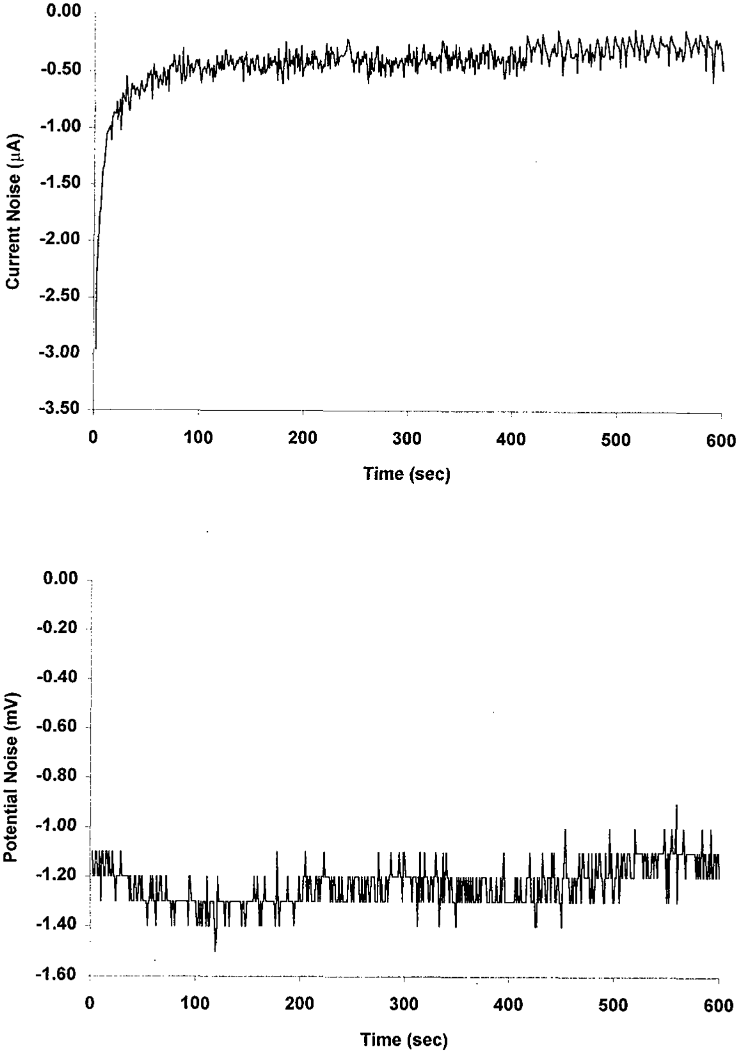


Figure 32: Raw current and potential from December 1996

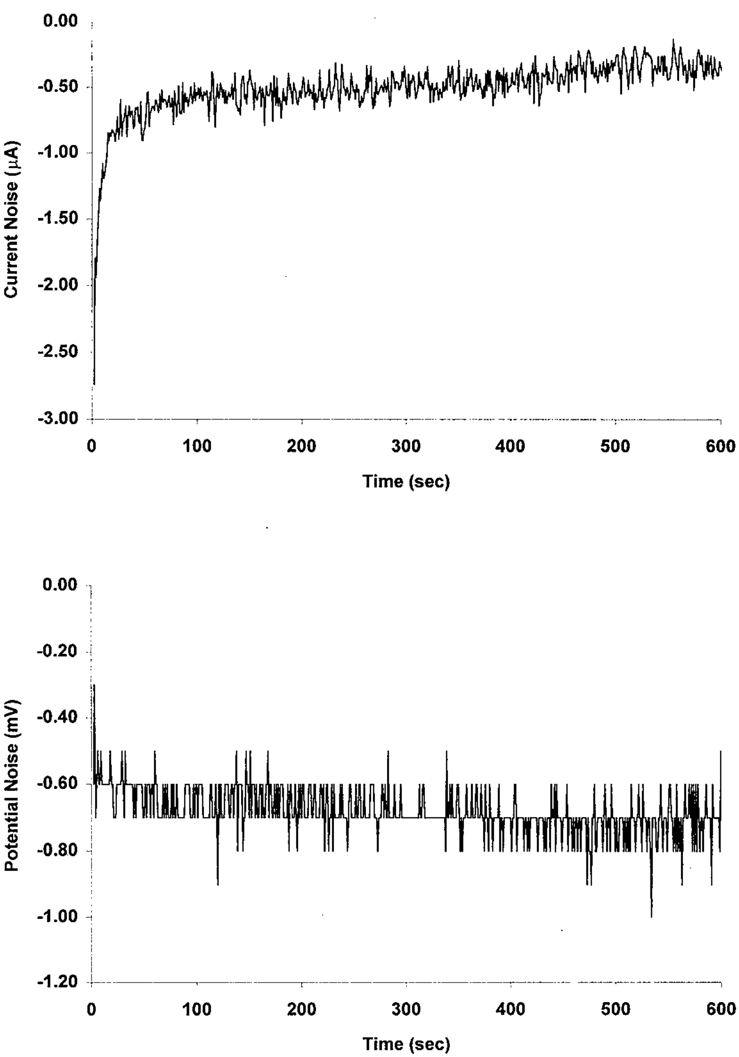


Figure 33: Raw current and potential from January 1997

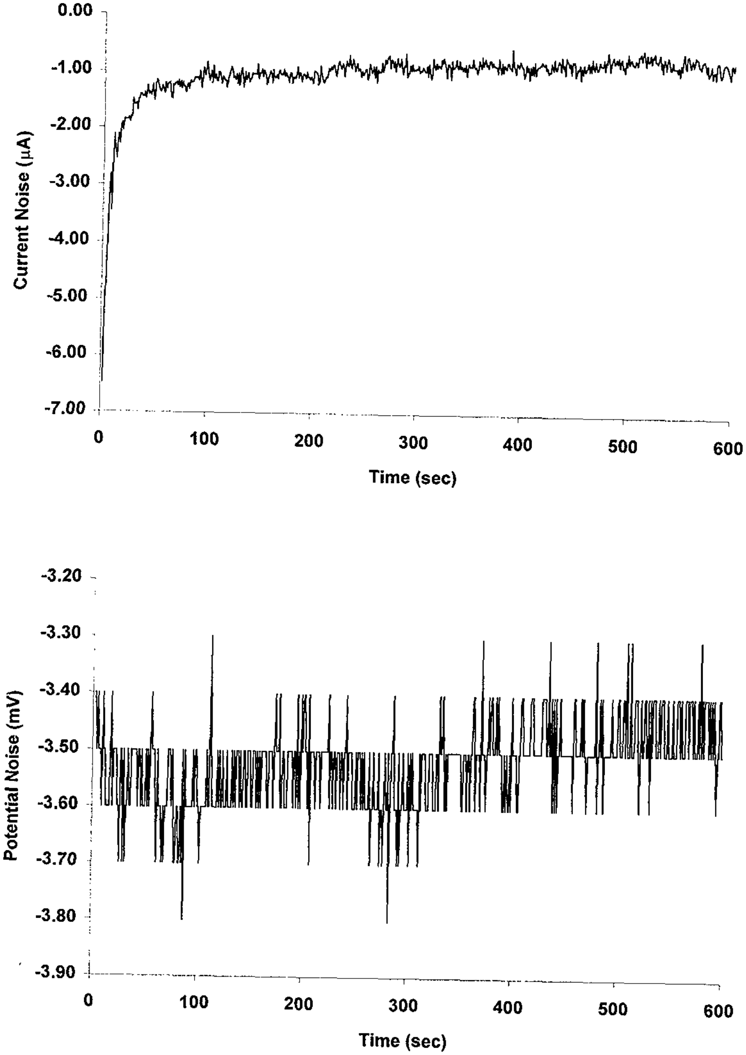


Figure 34: Raw current and potential from February 1997

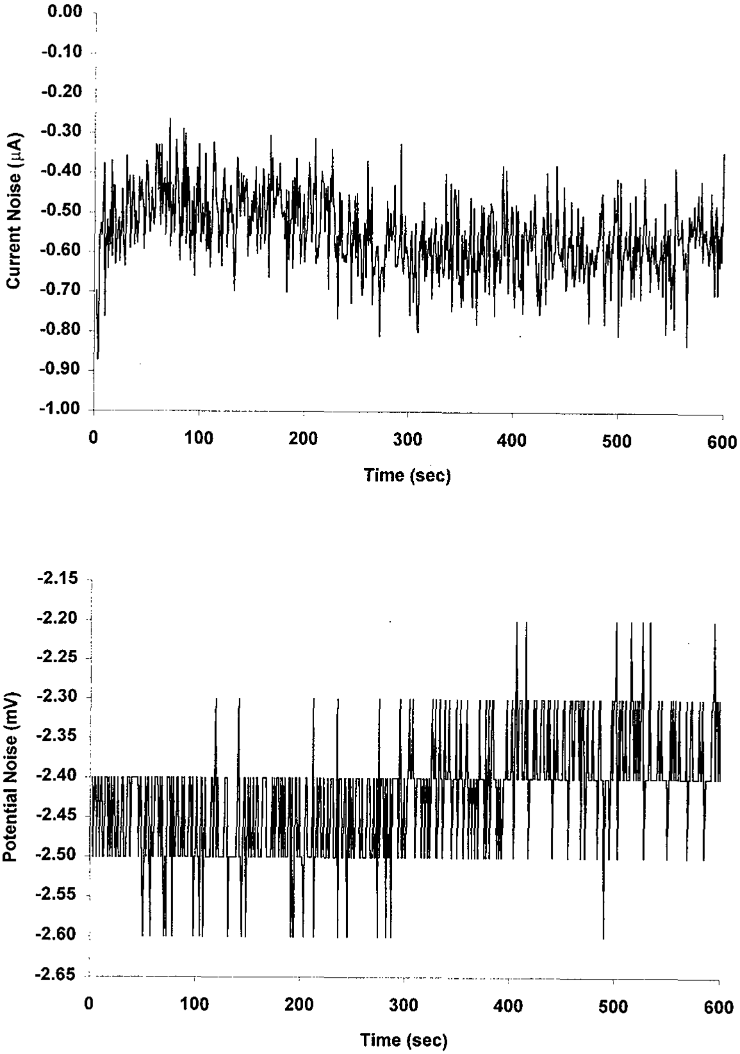


Figure 35: Raw current and potential from March 1997

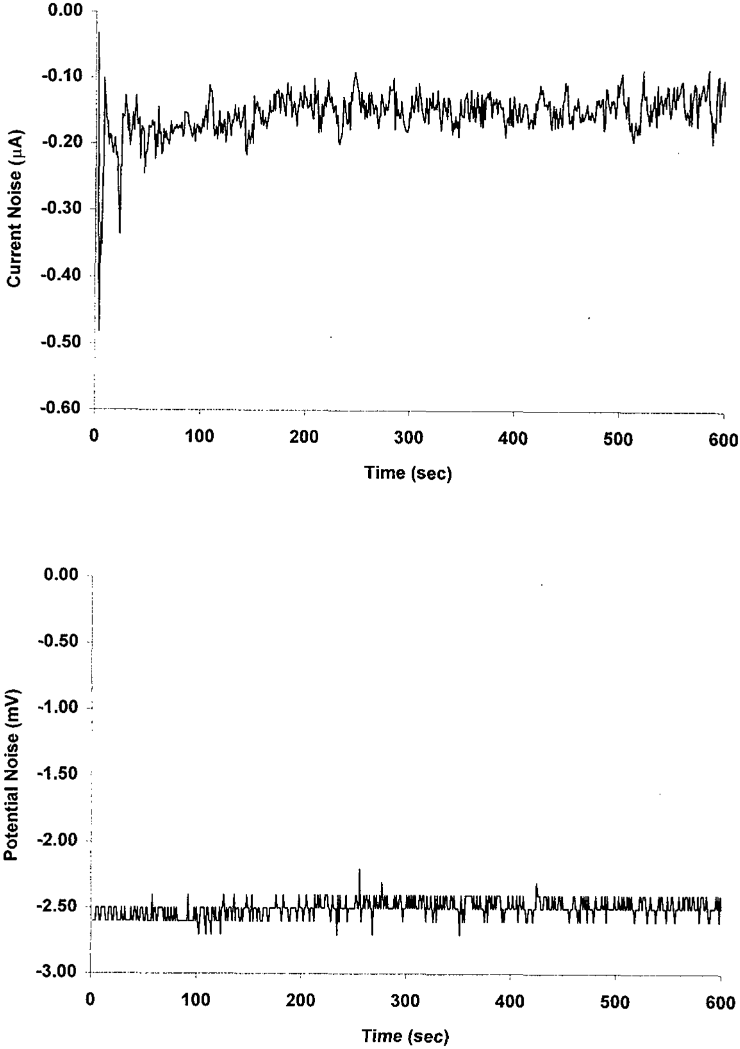
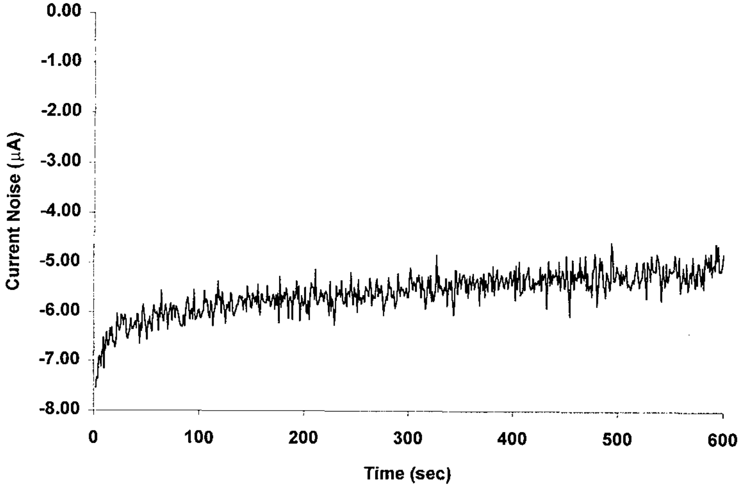


Figure 36: Raw current and potential from April 1997



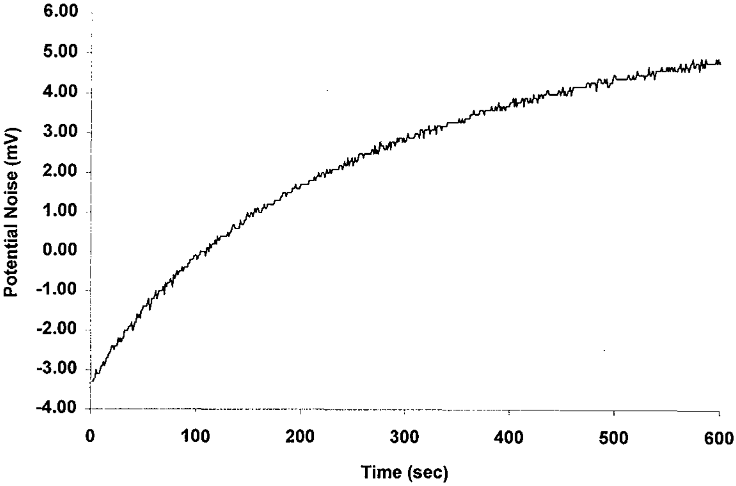


Figure 37: Raw current and potential from May 1997

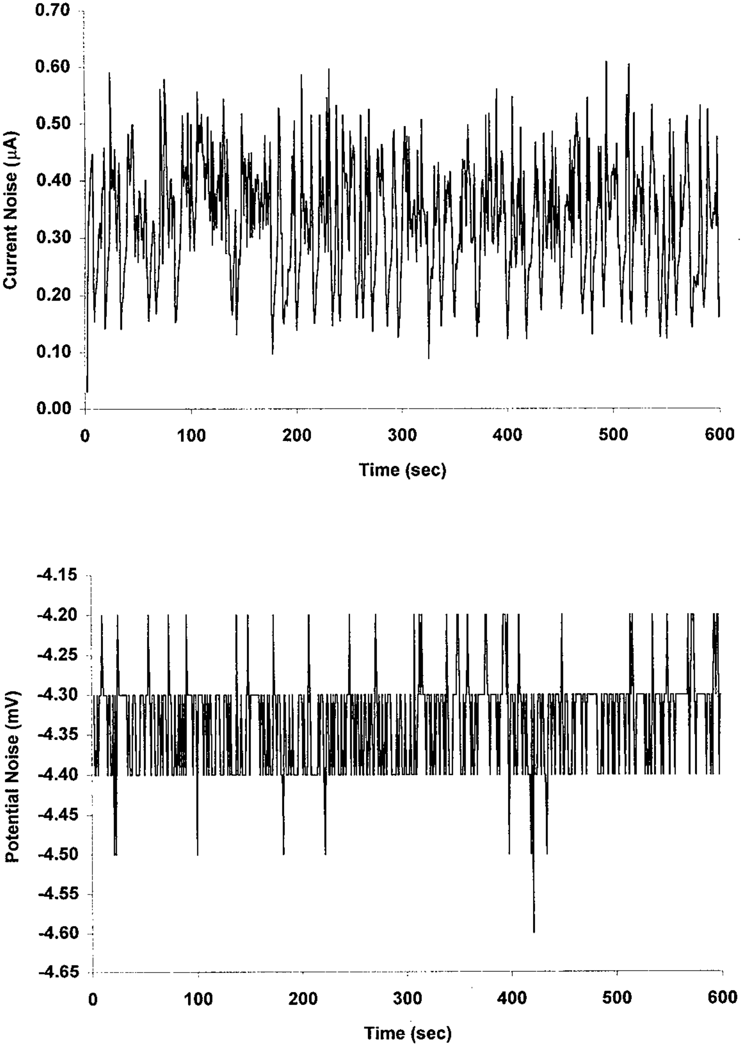


Figure 38: Raw current and potential from June 1997

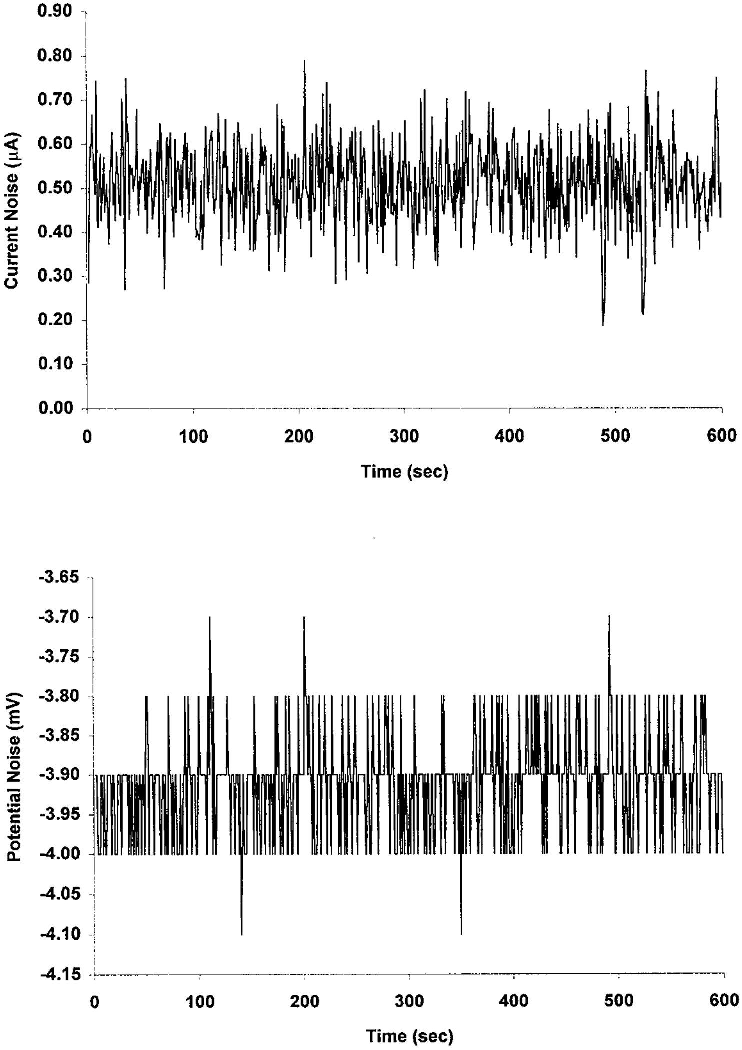
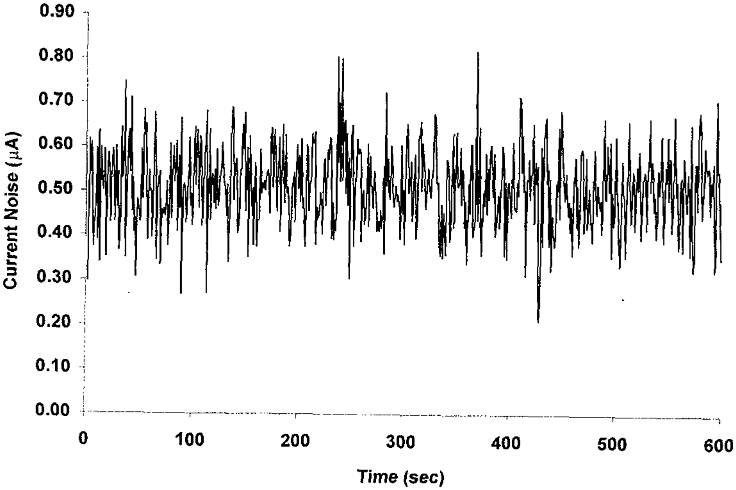


Figure 39: Raw current and potential from July 1997



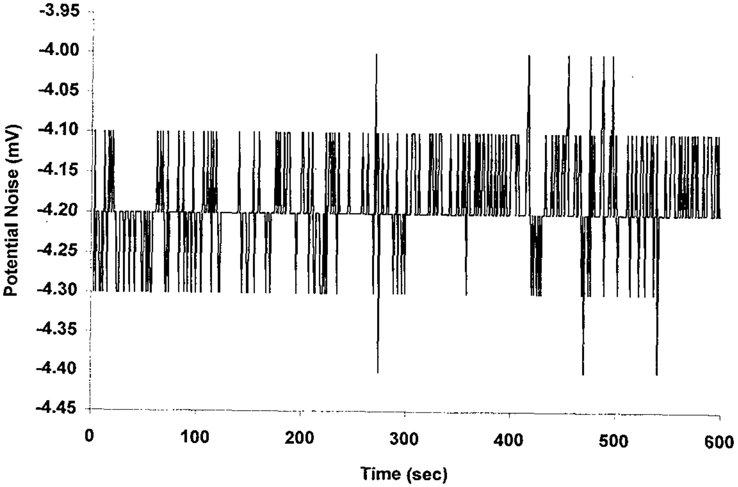


Figure 40: Raw current and potential from August 1997

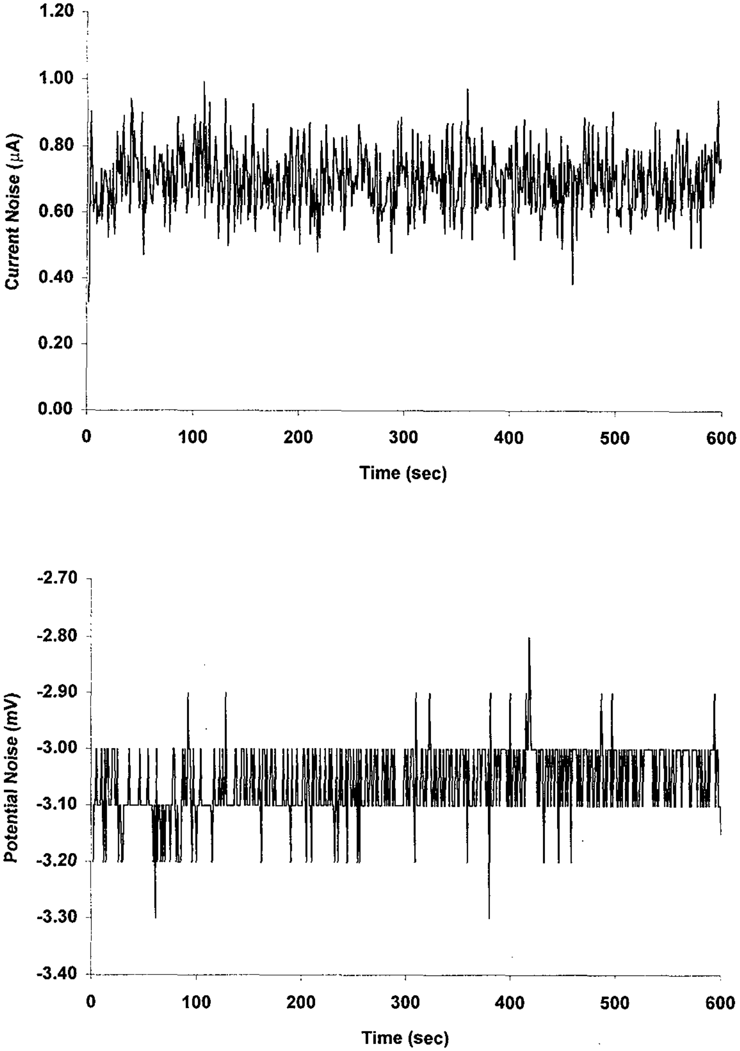
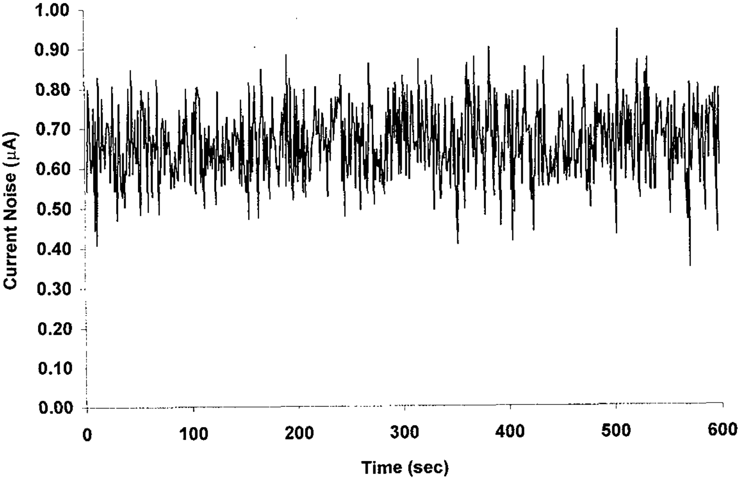


Figure 41: Raw current and potential from September 1997



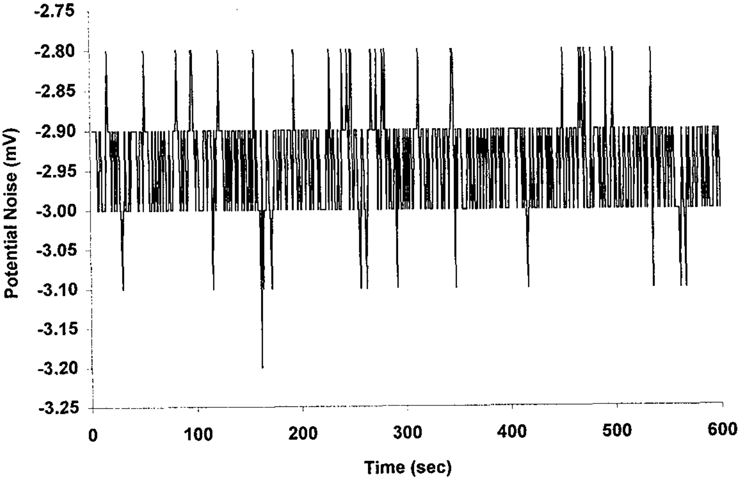


Figure 42: Raw current and potential from October 1997

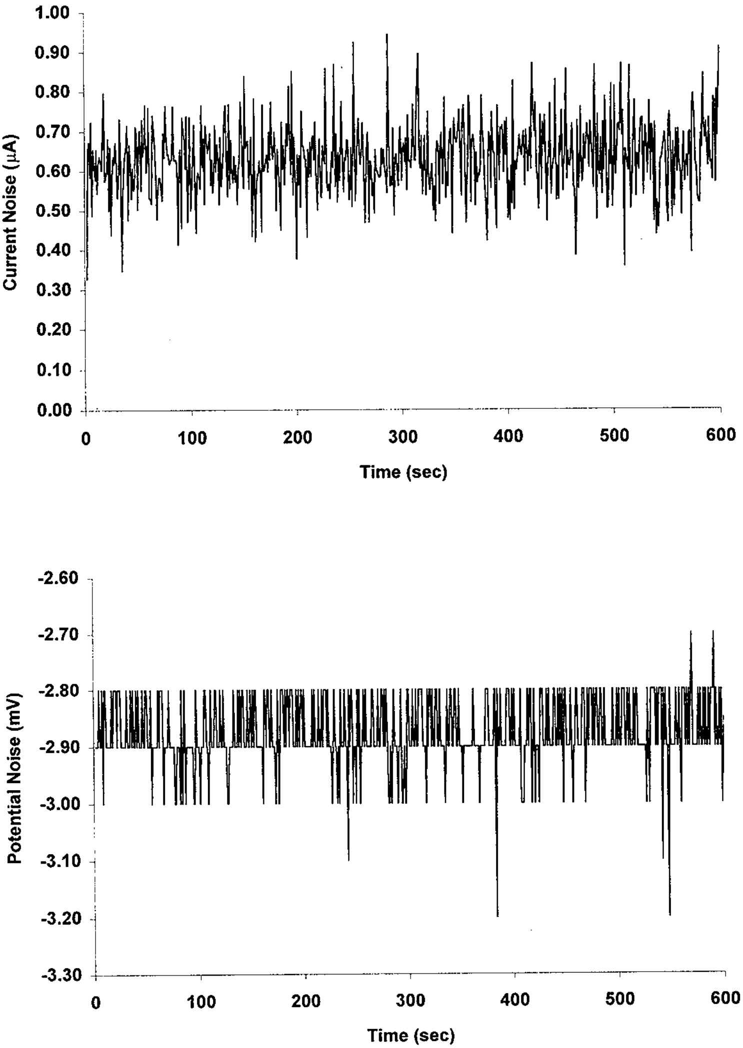
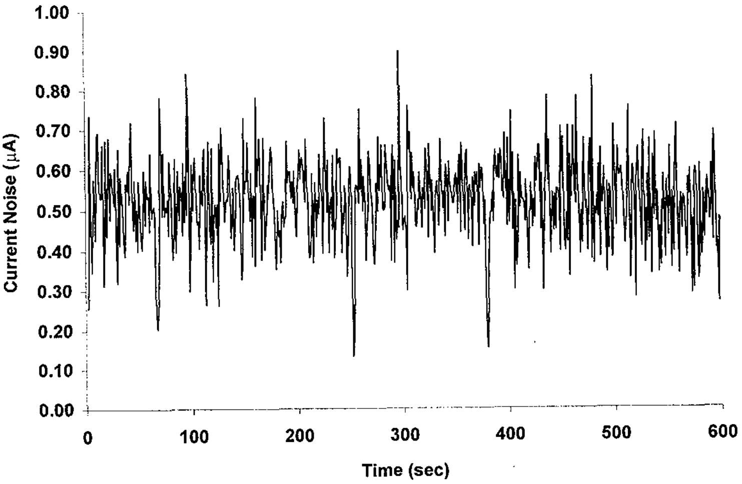


Figure 43: Raw current and potential from November 1997



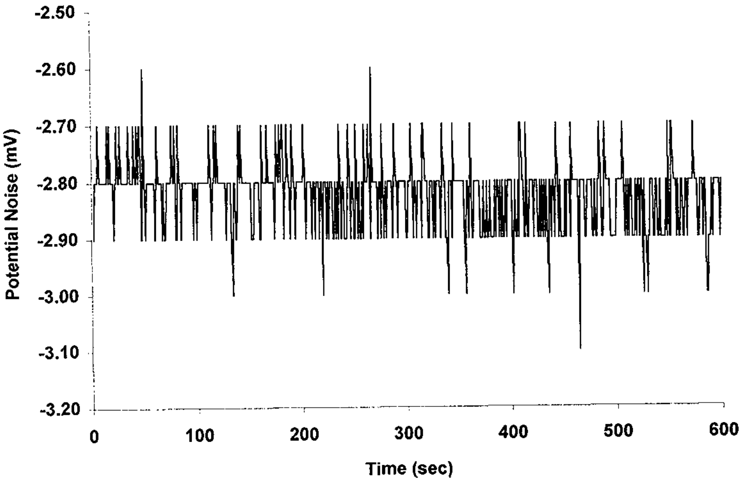
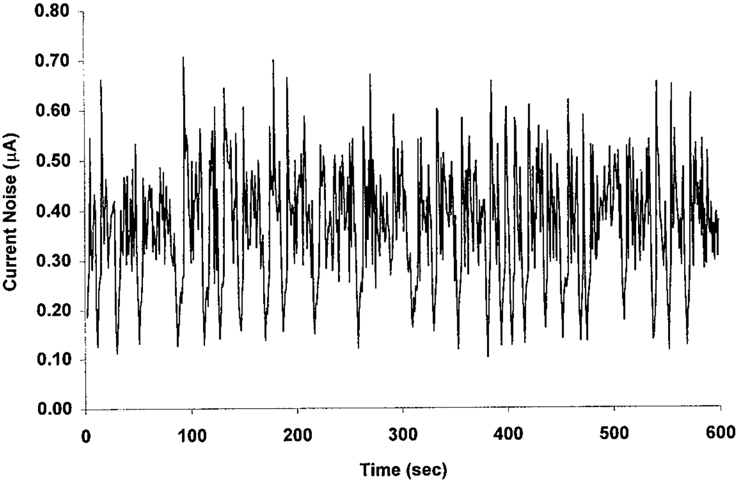


Figure 44: Raw current and potential from February 1998



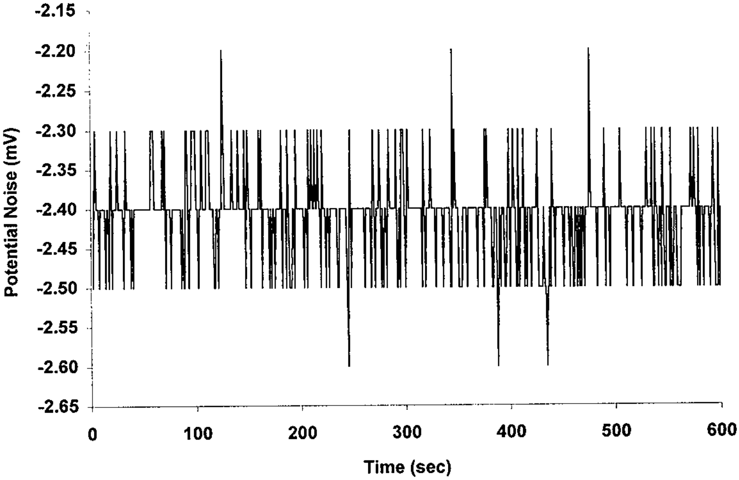
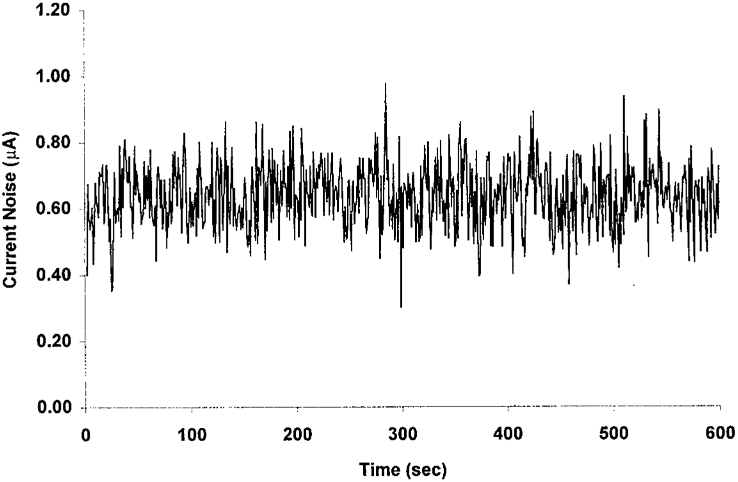


Figure 45: Raw current and potential from March 1998



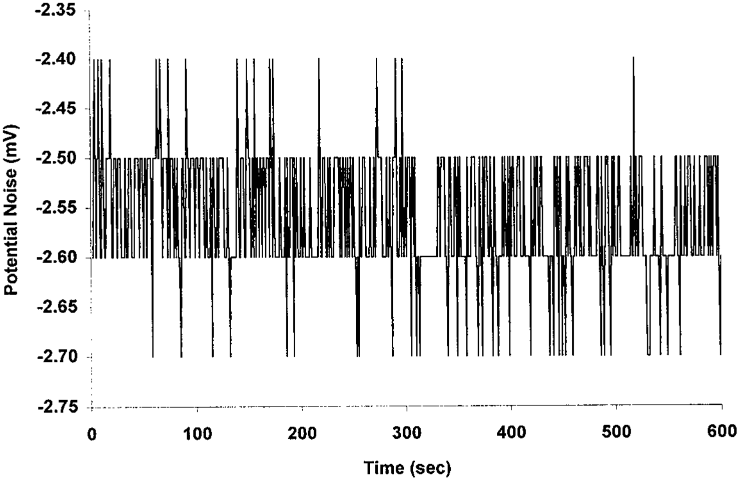
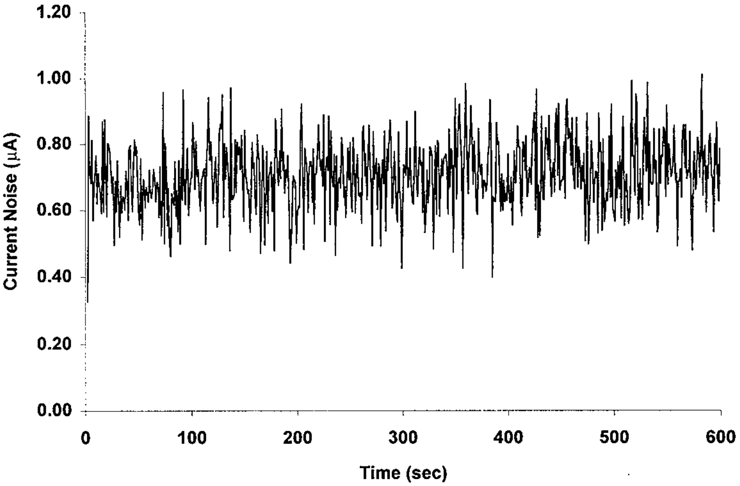


Figure 46: Raw current and potential from April 1998



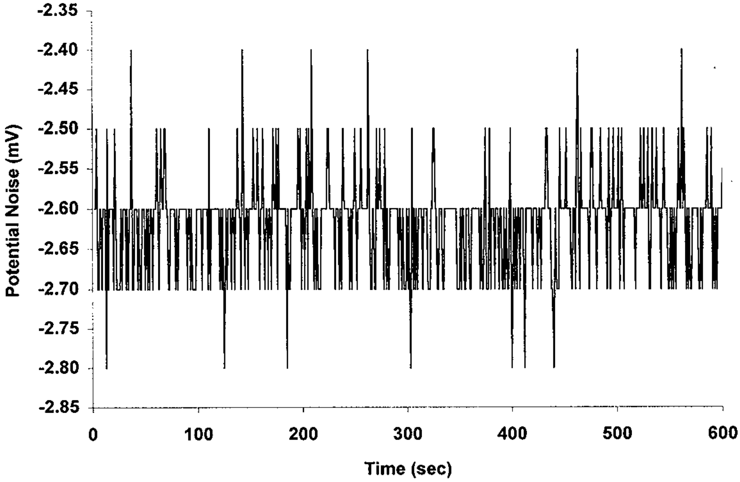
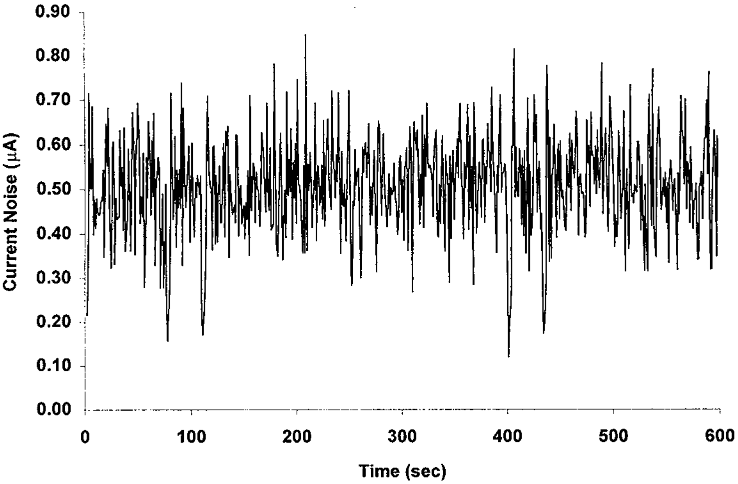


Figure 47: Raw current and potential from May 1998



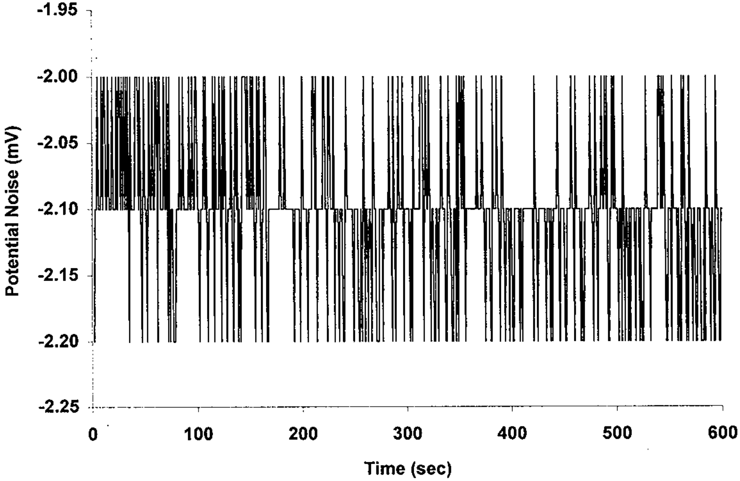
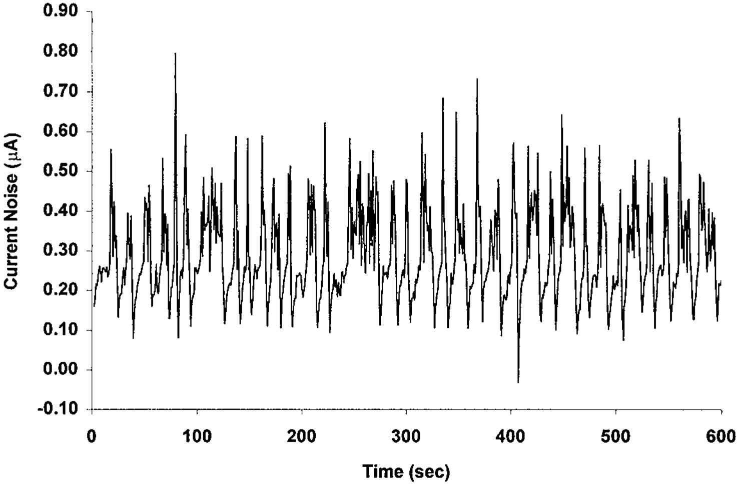


Figure 48: Raw current and potential from June 1998



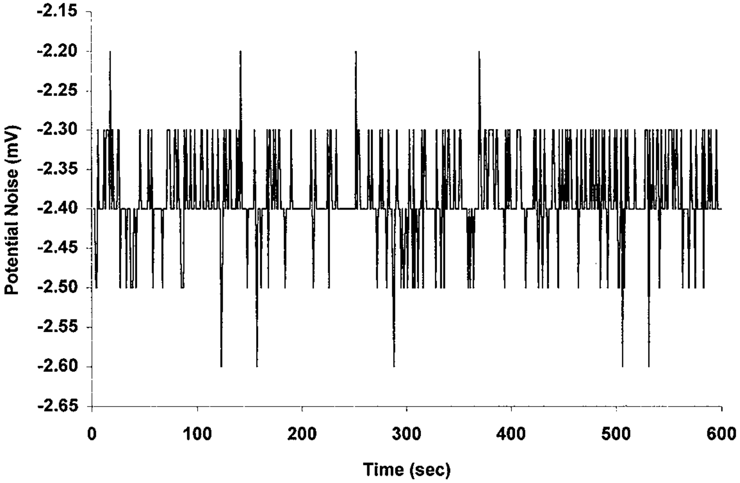


Figure 49: Raw current and potential from July 1998

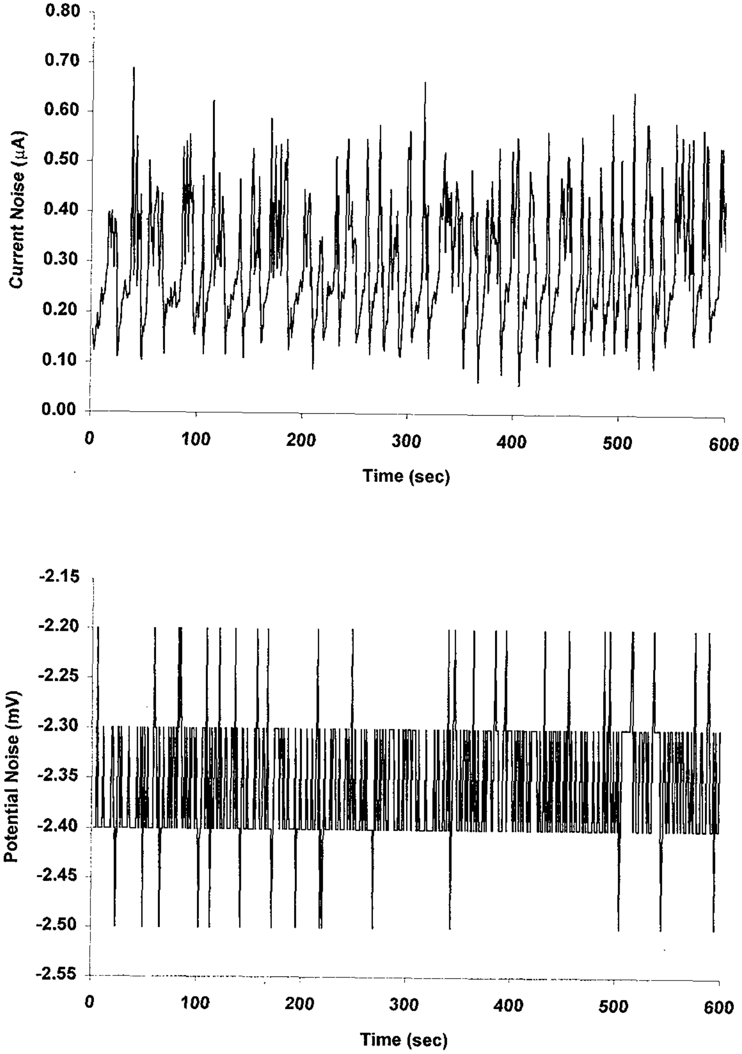


Figure 50: Raw current and potential from August 1998