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Attachell

Title: Voltage Noise Measurements on Sealed Lead Acid Batteries.

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Abstract:

// Voltage fluctuations observed during normal operation of sealed lead acid cells have given rise to an investigation on the potential of electrical noise monitoring as a characterization technique for specific problems associated with such sealed systems. The use of a cadmium reference electrode inserted in the mandrel of the Gates "J" type cells permitted to correlate different noise patterns with critical conditions of operation and assign them to either the positive or negative electrode. //

Résumé

L'observation de fluctuations du voltage durant l'opération normale de piles scellées plomb acide fut le point de départ d'une étude plus systématique ayant pour but de vérifier si l'analyse du bruit électrique pourrait permettre de caractériser certains problèmes typiques associés à la technologie de ces piles scellées. L'addition d'une électrode référence de cadmium dans le mandrin de piles Gates de type "J" a permis d'établir des corrélations utiles entre les patrons de bruit et certaines conditions critiques d'opération et d'associer le bruit à des problèmes provenant soit de la grille positive ou de la grille négative.

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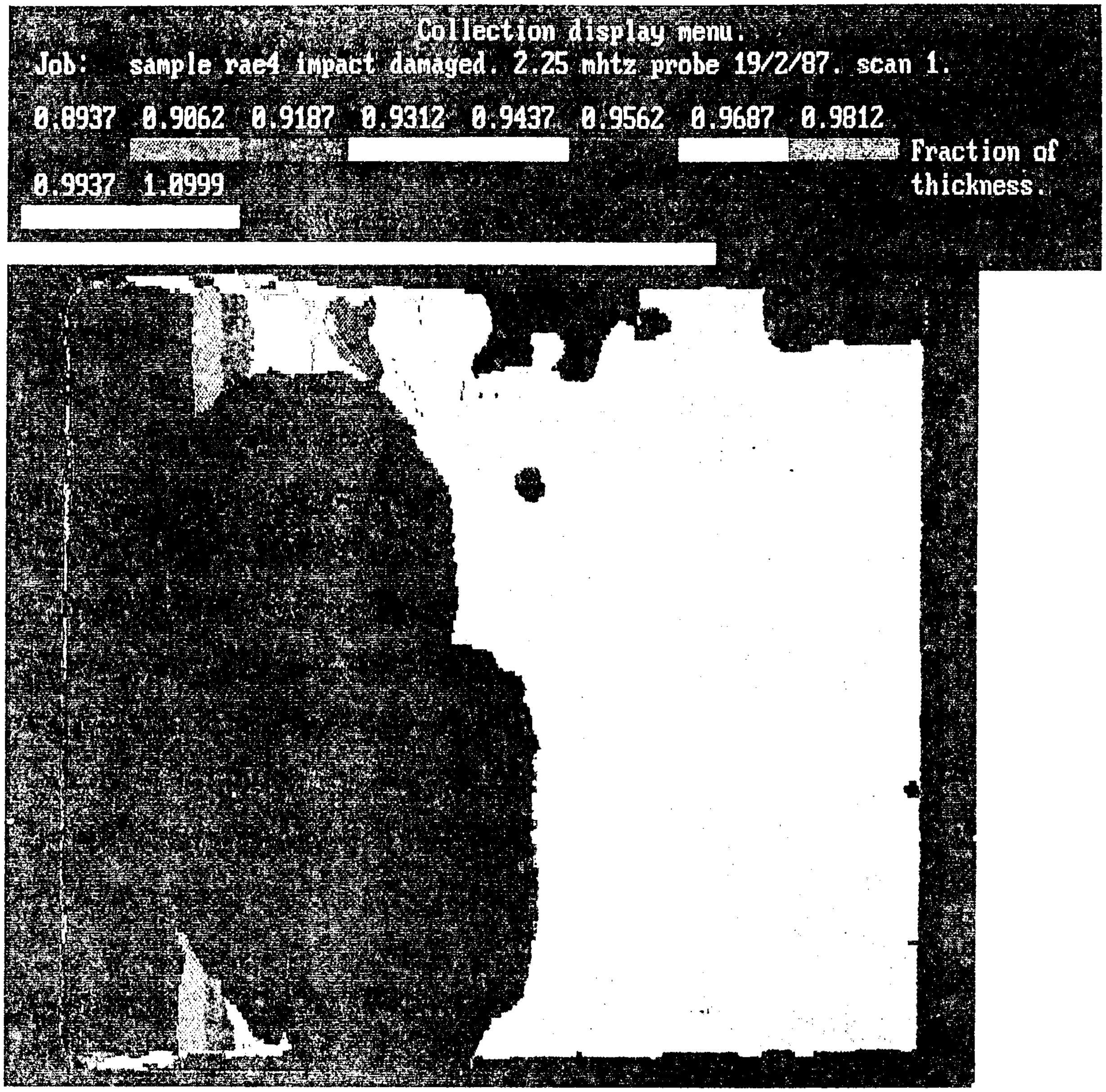


FIGURE 4.7 PLY BY PLY SCAN: PLIES 70-80

Colour thickness C-scan: Colour changes are set for increments of 1/80 of the sample thickness starting at 70.5/80 of the thickness. The black region which masks part of the scan is due to "damage" in plies 1–69. The band of coloured fringes near the edge of the specimen is the result of tapering thickness *Scale 71:100 reduced*

INTRODUCTION

Fluctuations in the current and potential signals of electrochemical systems usually referred to as electrochemical noise has long been of interest to electrochemists. Electrochemical noise studies carried on prior to 1972 have been reviewed by Tyagai [1]. More recent studies are reviewed in two subsequent publications [2,3]. Most of the noise work carried out to date has employed sophisticated data collection systems including correlation functions and spectrum analyzers [4,5] and has been associated with corrosion studies. Very limited research has been devoted to the study of noise measurement in battery systems [6,7]

Healthy fresh batteries are noiseless, but with use they can start to produce noise signals. Since most of the problem conditions leading to loss of battery performance tend to generate noise signals, the monitoring and analysis of the voltage noise patterns created during cell cycling could greatly enhance existing monitoring techniques.

Earlier reports [8,9] document some preliminary noise measurement data on Gates sealed lead acid cells. The noise patterns observed at the early stages of charging appeared to be related to charging difficulties at the positive electrode while noise patterns appearing at the end of charge were associated with problems at the negative electrode.

The origin of the noise signals from Gates sealed lead acid cells was confirmed through the use of a reference electrode. The present studies which employ the R.C. circuit used by Iverson [10], are being carried out to develop a simple noise measurement technique which can assist the battery shop in predicting the state of health of a battery.

This paper analyzes the techniques used and presents in detail the noise data generated while charging both healthy and defective Gates (USA) "J" Type - 7.5Ah cells.

EXPERIMENTAL

Figure 1 is a schematic diagram of the system used to monitor voltage noise patterns. The system consists of a charge-discharge circuit and an RC measuring circuit in which a 1 megaohm resistor (R) and 1 microfarad capacitor (C) are used in series to block the DC voltage of the cell (P) under study. The current circulating through the RC circuit is monitored by measuring the voltage drop across the resistor with a 5 1/2 digit voltmeter.

To prevent any instrumental interference in the charge-discharge circuit (power supply, line voltage, etc.) the charging power comes from two fully charged 315 Ah Sonnenschein cells (E_1) connected in series with a purely resistive circuit. The load resistance (R_L) controls the current level and the voltage drop across a shunt resistance (R_S) is used to monitor it. All the data are stored by a computer for later manipulation and can be viewed live on a chart pen recorder.

The cadmium reference electrode was wrapped in a piece of separator material wetted with H_2SO_4 and inserted into the hollow cell mandrel. The electrical contact with the reference electrode was achieved by firmly crimping a small diameter (2 mm) copper rod to the cadmium electrode. Care was taken to preserve the original hermetic character of the cells by letting the copper wire go through directly the tightly fitting rubber vent cap.

RESULTS

Figure 2 depicts noise obtained from a healthy cell while being charged and discharged at 7A. The data illustrates that under normal operating conditions the cell did not produce any significant noise.

In order to study the noise pattern produced by a less than healthy cell, the cell used to obtain fig. 2 was discharged down to zero volt and left on short-circuit for 20 hours. Fig. 3 illustrates the noise pattern obtained from this cell while being recharged at 0.5A. The high intensity spikes suggest that the cell is undergoing rapid voltage fluctuations during its constant current charging. This test was duplicated on another cell in which a reference cadmium electrode was introduced to measure the noise at the positive and at the negative electrodes. Fig. 4 illustrates the noise pattern sampled at 5 minute intervals at the various electrodes during the recharge of the cell. The cell noise was found to be identical to the noise originating from the positive electrode while the negative electrode contributed no noise. The background noise measured across the charging circuit shunt was found to be negligible.

Figure 5 illustrates another noise pattern encountered during our study. Some cells charged at or above the gas evolution potential (over 2.30 volts) produced noise characterized by a majority of negatively directed peaks. This type of noise illustrated in fig. 6 originates from the negative electrode and has been linked to problems at the negative electrode.

In an earlier paper it was reported that Gates "J" cells had on occasion developed high impedance problems at the positive and negative posts [8]. To eliminate this as a possible source of noise the posts were bypassed by screwing two connectors directly into the tabs of the electrode plates as illustrated in fig. 7. Noise data collected from the original post was compared to that collected from the added connectors. The similarity of the two sets of noise data as illustrated in fig. 8 suggests that the noise pattern was the result of a phenomenon occurring at the electrodes. A significant difference in the noise pattern was noted once the screw connectors became corroded. Fig. 9 illustrates the noise signal measured at the screw connectors after one week of testing. This noise is characterized by a fine structure of positively directed peaks occurring at regular intervals.

Figs. 10 to 12 display on a constantly expanded time scale the three types of noise discussed. The noise at the positive electrode appears as finely structured randomly distributed peaks with no bias in the direction of the peaks while the noise at the negative electrode consists of peaks that are negatively biased. The noise generated at the corroded screw connector appears as randomly spaced positively biased spikes on a noiseless background.

DISCUSSION

The noise data can be explained by interpreting the current circulating in the RC circuit below its cut off frequency as a function of the cell voltage which is responsible for the general shape of the trace, with the current fluctuations above the cut off frequency being responsible for the characteristics of the noise.

The general shape of the noise curves illustrated in fig. 2 is similar to the charge-discharge curves. However, a major difference can be noted when the external source voltage is initially applied. The curve of the noise signal is characteristic of the derivative of the cell voltage and is therefore radically affected by the initial response of the cell voltage to an external source. A change in sign of (dEp)/(dt) causes a change in the direction of the current in the RC circuit resulting in wild fluctuations in the noise traces. Following these initial excursions the cell voltage generally stabilizes producing a broad plateau on the noise curves. Near the end of the charge (dEp)/(dt) starts to increase gradually. A similar correlation can be used to explain the general shape of the discharge curve.

Assuming that the current fluctuations observed on the plateaus are principally caused by fluctuations of the internal resistance of the cell being tested, it is possible to estimate the relative sensitivity of this technique to such variations. For a typical internal resistance of 3 milliohms and a charging current of 7A, the ohmic loss would be nominally 21 mV. In such a case, transients of 0.1 mV on the noise recordings would represent corresponding variations of approximately 0.25% of the internal resistance of a cell.

The main data presented correlates well with the present understanding of phenomena that can occur in sealed lead acid batteries. Cells built with non antimonial positive grids develop an insulating layer on the grids when left in a discharged state for an extended period of time. The subsequent charging problem [11] is illustrated in fig. 3 which depicts a noise signal generated at the positive electrode. This noise disappeared with cycling or extended charging. Gas samples were taken with a syringe while this early stage of charging noise was generated. The analysis of these samples by gas chromatography did not reveal any significant increase in either oxygen or hydrogen thus ruling out gas evolution as a probable cause of this type of noise usually also associated with the positive electrode. Noise signals tend to be generated at the negative electrode in cells where low capacity is a result of a performance deterioration of the negative plate. The width and direction of the noise peaks suggest a possible problem in the oxygen recombination process. This negative electrode noise which does not disappear with cycling has not been fully interpreted and is the object of further studies.

CONCLUSION

While a more complete explanation for the noise patterns is still being sought, it can already be concluded that the voltage noise produced in normal conditions of operation is a valid indicator of potential cell or battery problems. Since the monitoring technique does not, in itself, require a sophisticated level of instrumentation, it would be relatively easy for a battery shop to adopt it provided a solid correlation is established between battery problems and observed noise patterns.

REFERENCES

1. V.A. Tyagai, Elektrokhimiya 10 (1974) 3.

2. A. Bezegh and J. Janata, Anal. Chem. 59 (1987) 494A.

3. P.C. Searson and J.L. Dawson, J. Electrochem. Soc. 135 (1988) 1908.

4. G. Blanc, C. Gabrielli and M. Keddam, Electrochim. Acta 20 (1975) 687.

5. U. Bertocci, J. Electrochem. Soc. 128 (1981) 520.

6. K.F. Knott, Electron. Letters 1 (1965) 132.

7. A. Chabli, J.P. Diard, P. Landaud and B. LeGorrec, Electrochim. Acta 29 (1984) 509.

8. G. Verville, P. Roberge and J. Smit, Power Sources 12, in press.

9. G. Verville, P. Roberge, R. Beaudoin and J. Smit. Proc. of the 9th International Electric Vehicle Symposium, EVS88-060, 13-16 Nov. 1988, Toronto.

10. W.P. Iverson, J. Electrochem. Soc. 115 (1968) 617.

11. H.K. Giess. Proceedings of the Symposium on Advances in Lead Acid Batteries, edited by K.R. Bullock, D. Pavlov. Electrochemical Society Proceedings volume 84-14, 241.

Fig. 1 Experimental set-up for noise measurement. R = 1 MegaOhm; C = 1 microFarad; P = cell under test; R_s = shunt resistance; R_L = load resistance; E_1 = power source batteries.

Fig. 2 Noise patterns of a healthy Gates "J" sealed lead acid cell while on charge and discharge at 7 A.

Fig. 3 Noise patterns of a noisy Gates "J" sealed lead acid cell while on charge at 0.5A.

Fig. 4 Noise patterns of a noisy Gates "J" sealed lead acid cell while on charge at 0.5A and observed at different locations: a) total cell; b) positive electrode; c) negative electrode; d) shunt resistance.

Fig. 5 Noise patterns obtained with a cell exhibiting noise in the overpotential region; a) charging at 7.5 A; b) charging at 2 A.

Fig. 6 Noise patterns measured at different locations during the charging process at 2 A in the 2.3 Volts domain; a) section between 2.28 and 2.31 Volts from Fig. 5; b) positive electrode; c) negative electrode, between 2.28 and 2.31 Volts; d) shunt resistance.

Fig. 7 Additional connectors directly in contact with the collectors of a Gates "J" sealed lead acid cell.

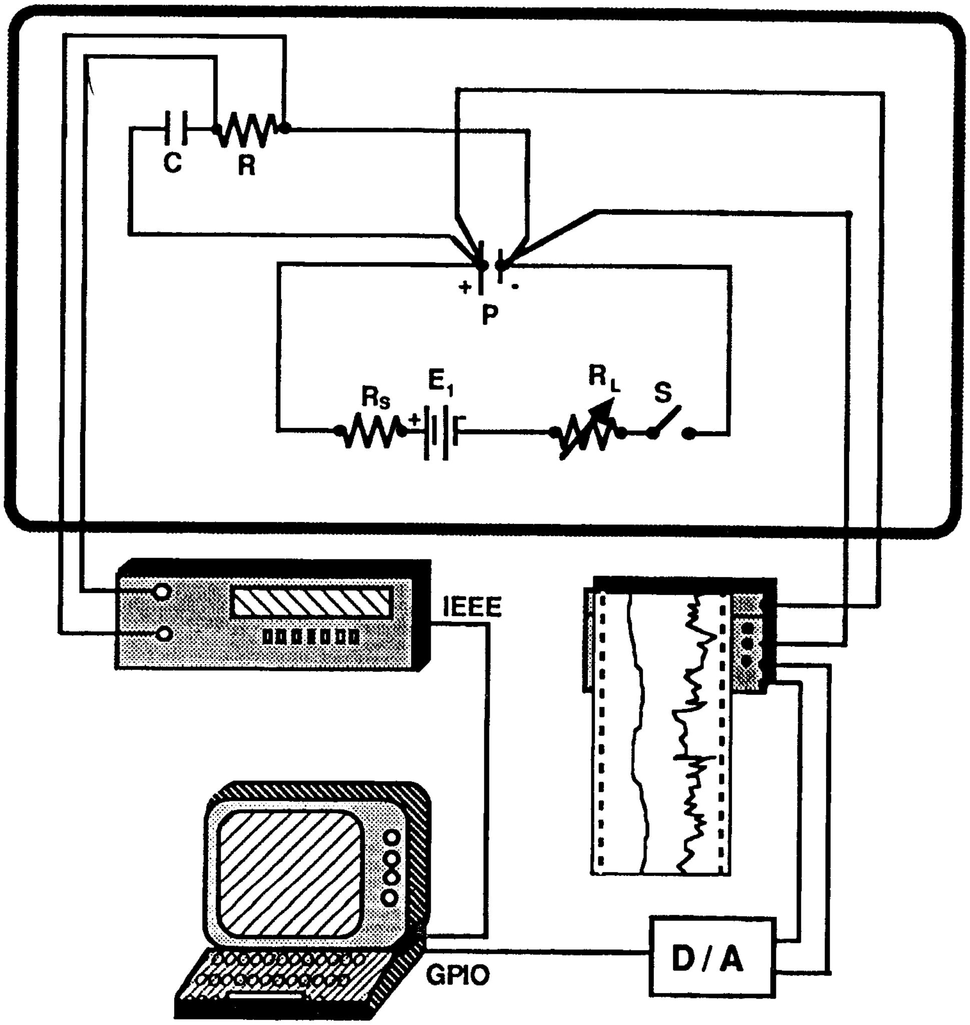
Fig. 8 Noise patterns while on charge at 7A and coming; a) from the original posts; b) from added connectors.

Fig. 9 Noise patterns while on charge at 7A and coming from the added connectors after one week.

Fig. 10 Time scale expansion of typical noise generated at the positive electrode for a cell being charged at 0.5A.

Fig. 11 Time scale expansion of typical noise generated at the negative electrode for a cell being charged at 7A.

Fig. 12 Time scale expansion of typical noise generated from added screw connectors after one week and while on charge at 7A.


C
R
+
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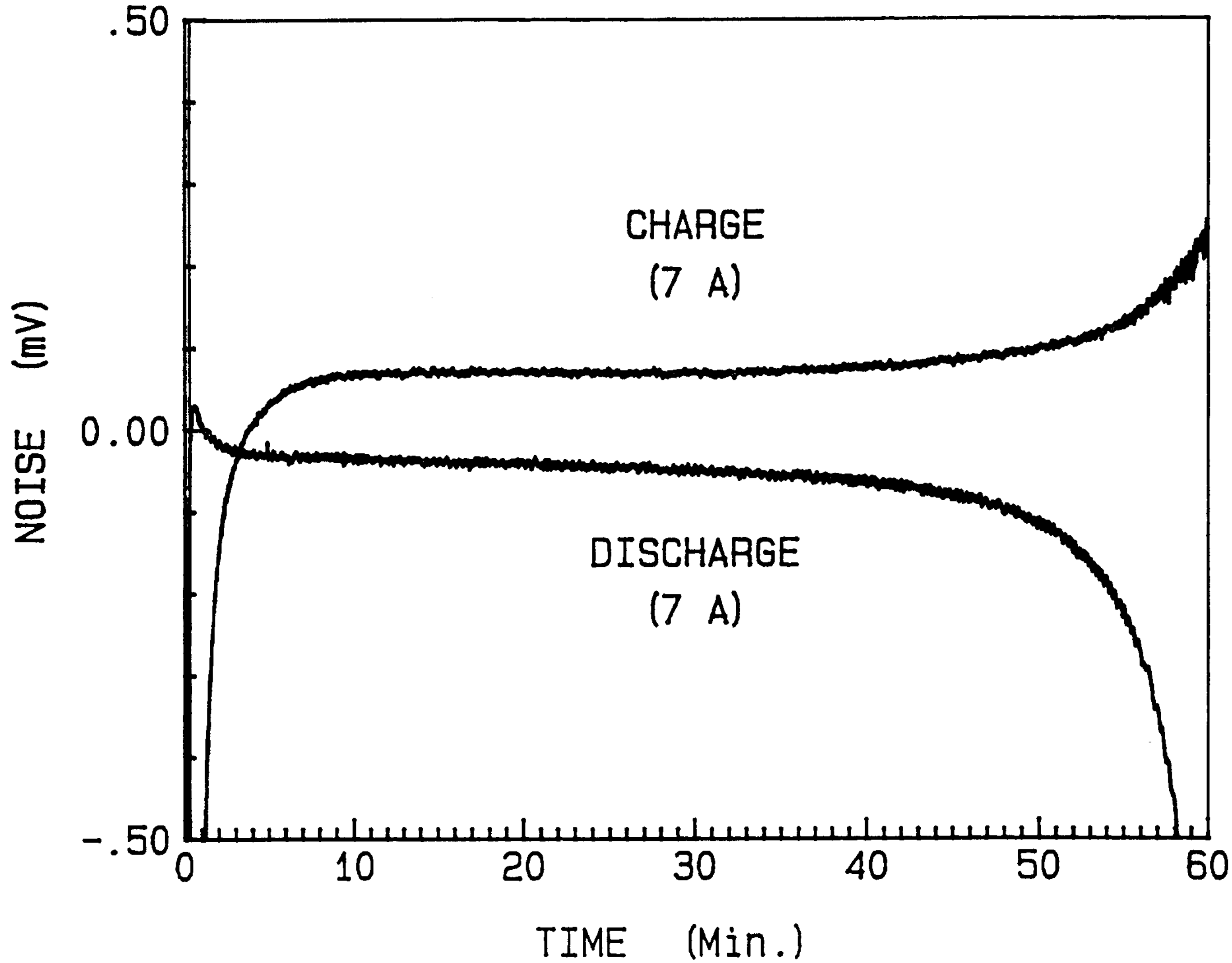
GPIO



.50
0.00
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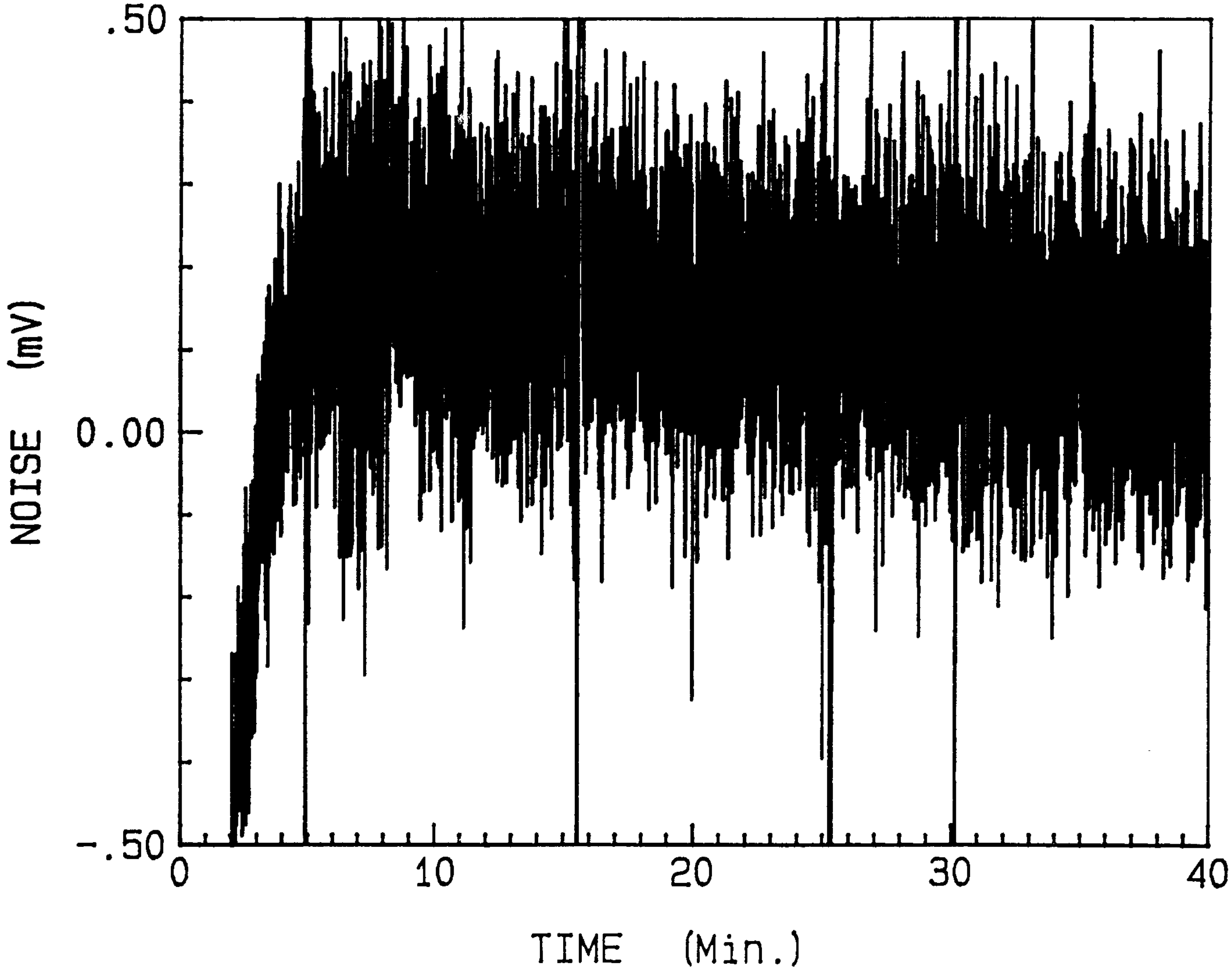
NOISE (mV)
CHARGE
(7 A)
DISCHARGE
(7 A)
0
10
20
30
40
50
60
TIME (Min.)



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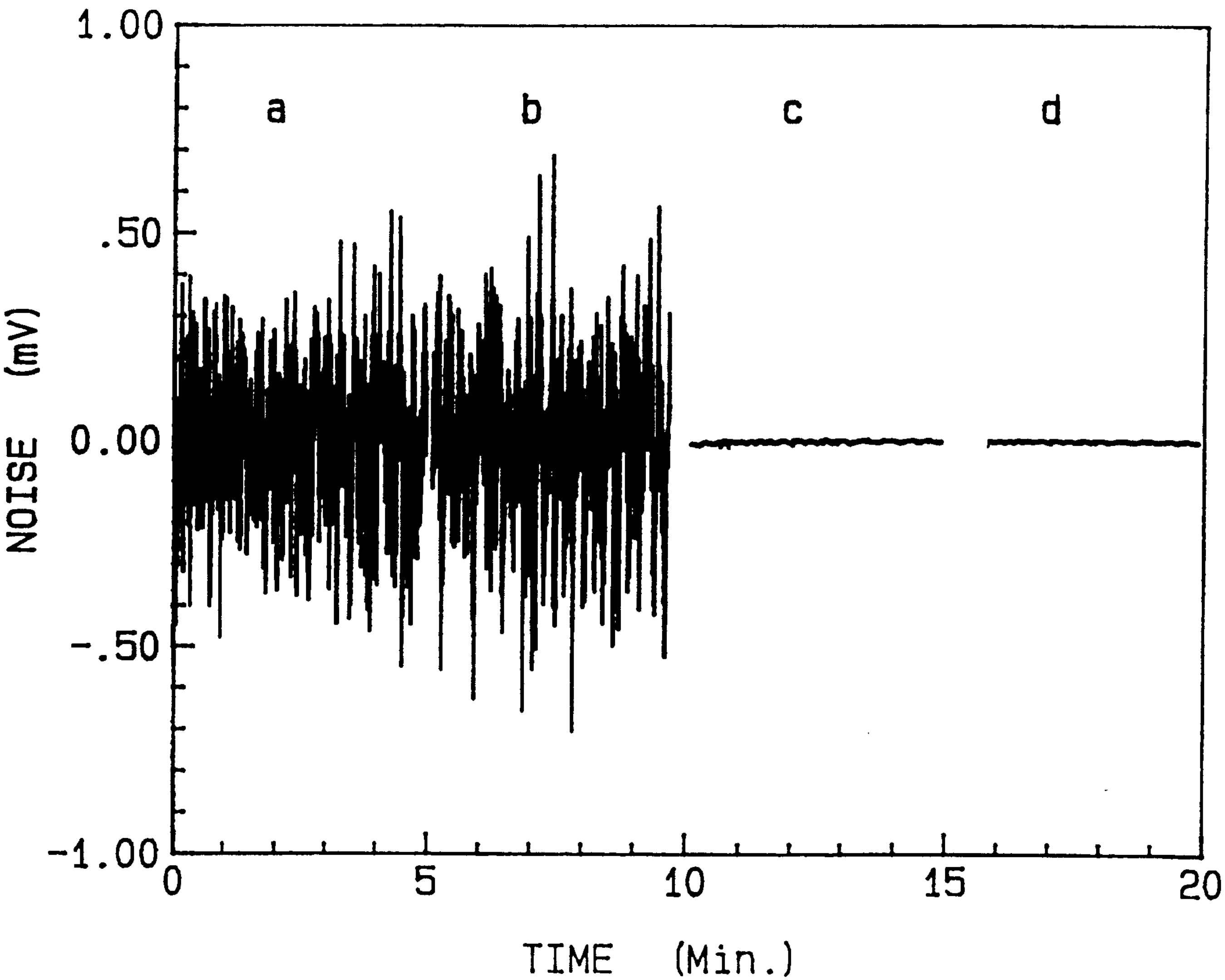
0.00
-.50
NOISE (mV)
0
10
20
30
40
TIME (Min.)



a
b
c
d
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0.00
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-1.00
NOISE (mV)
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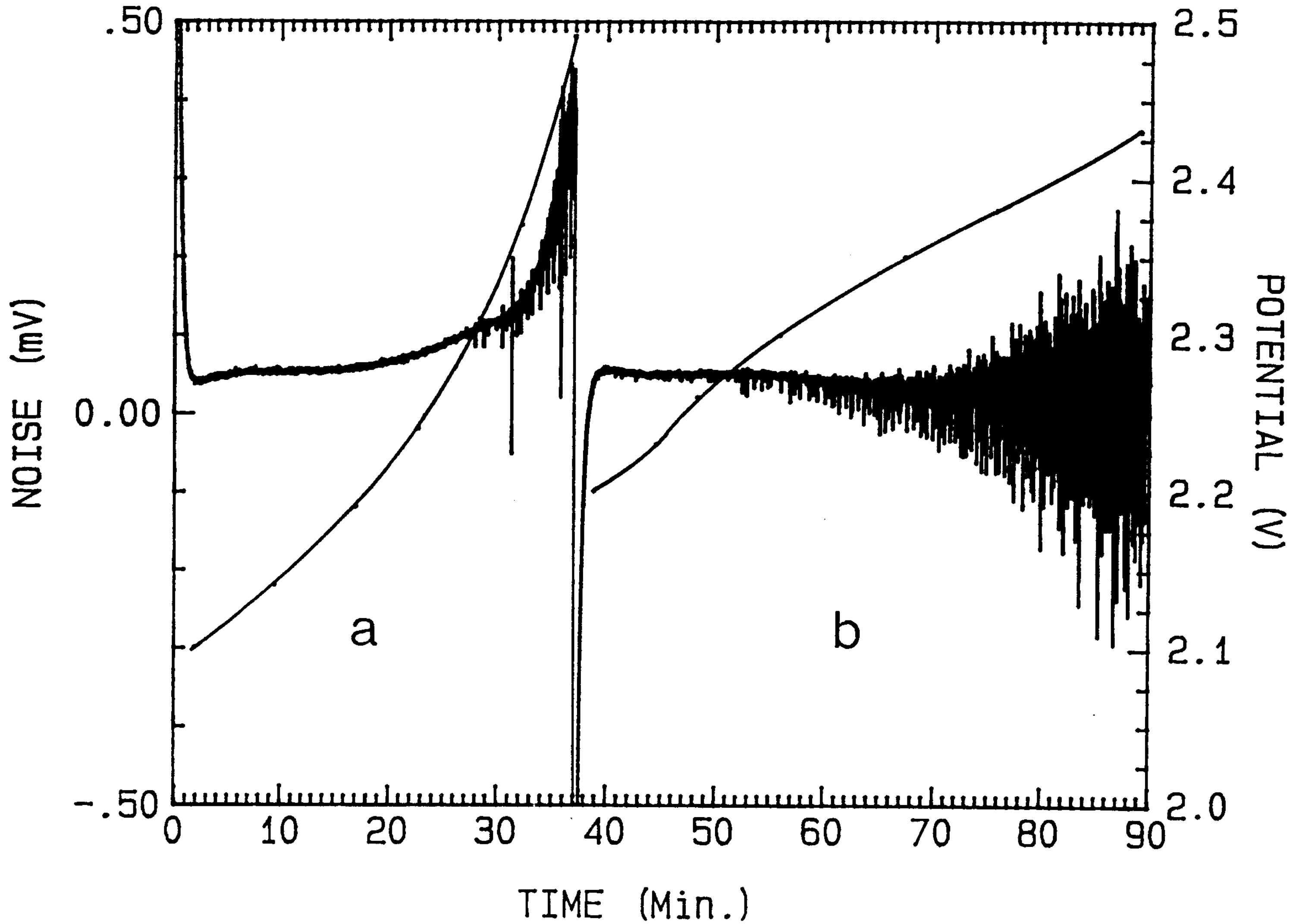
5
10
15
20
TIME (Min.)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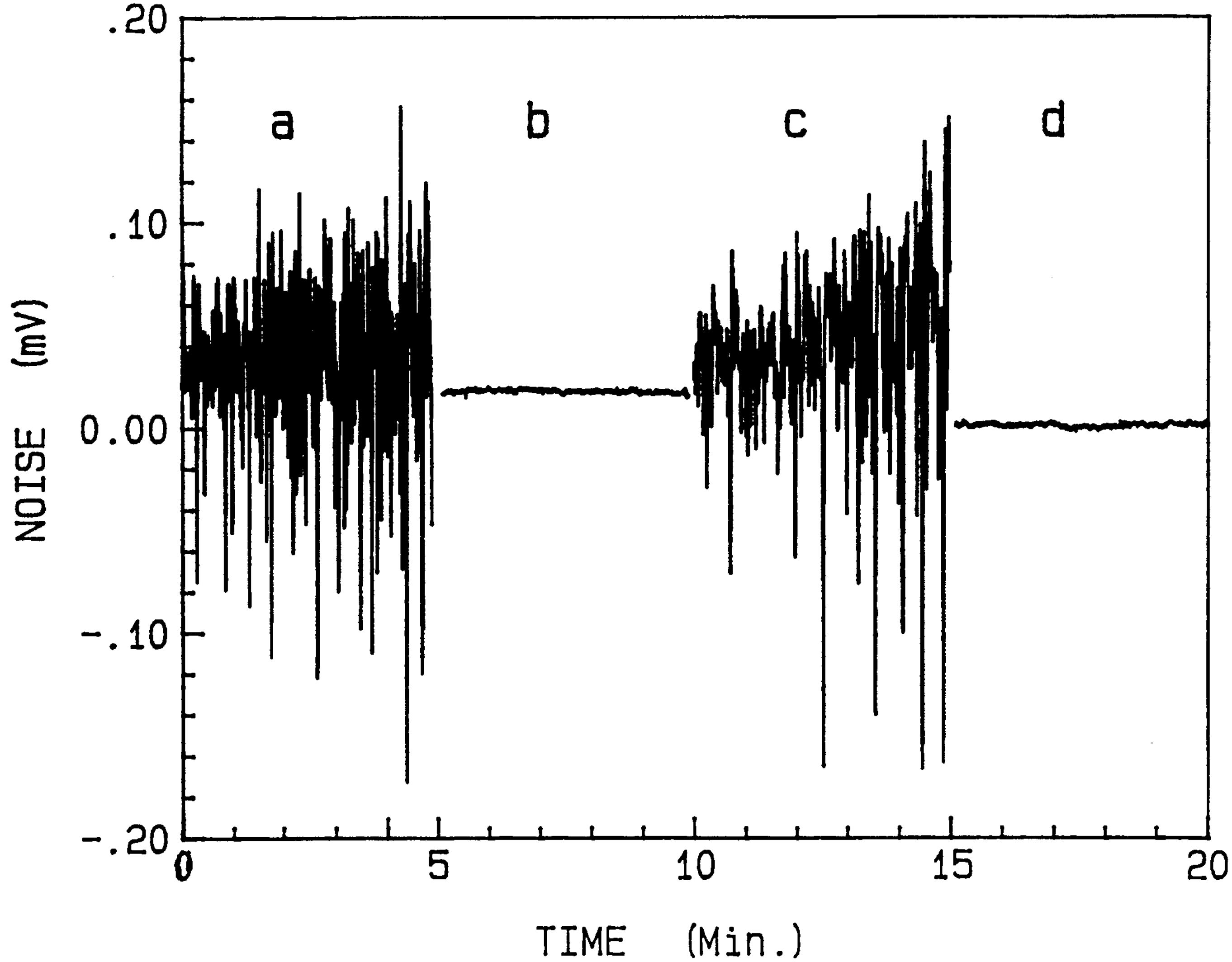
20
30
40
50
60
70
80
90
TIME (Min.)
a
b



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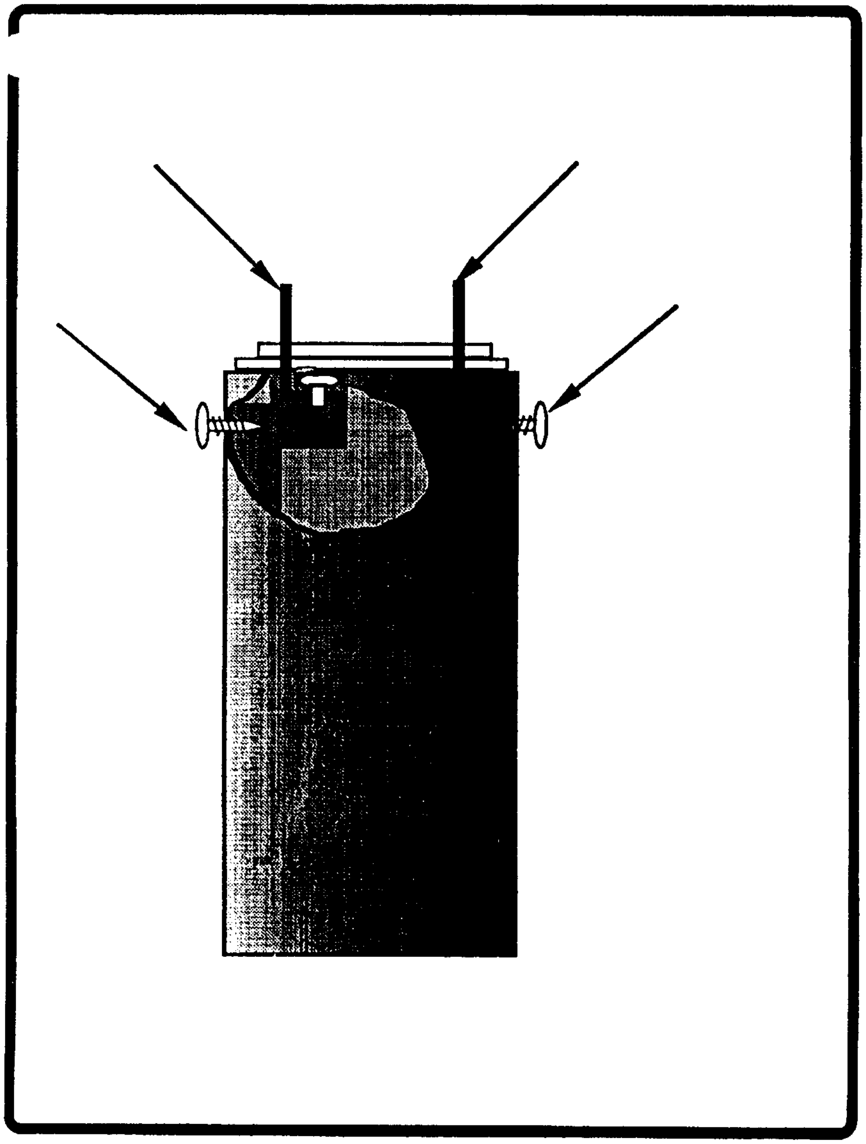


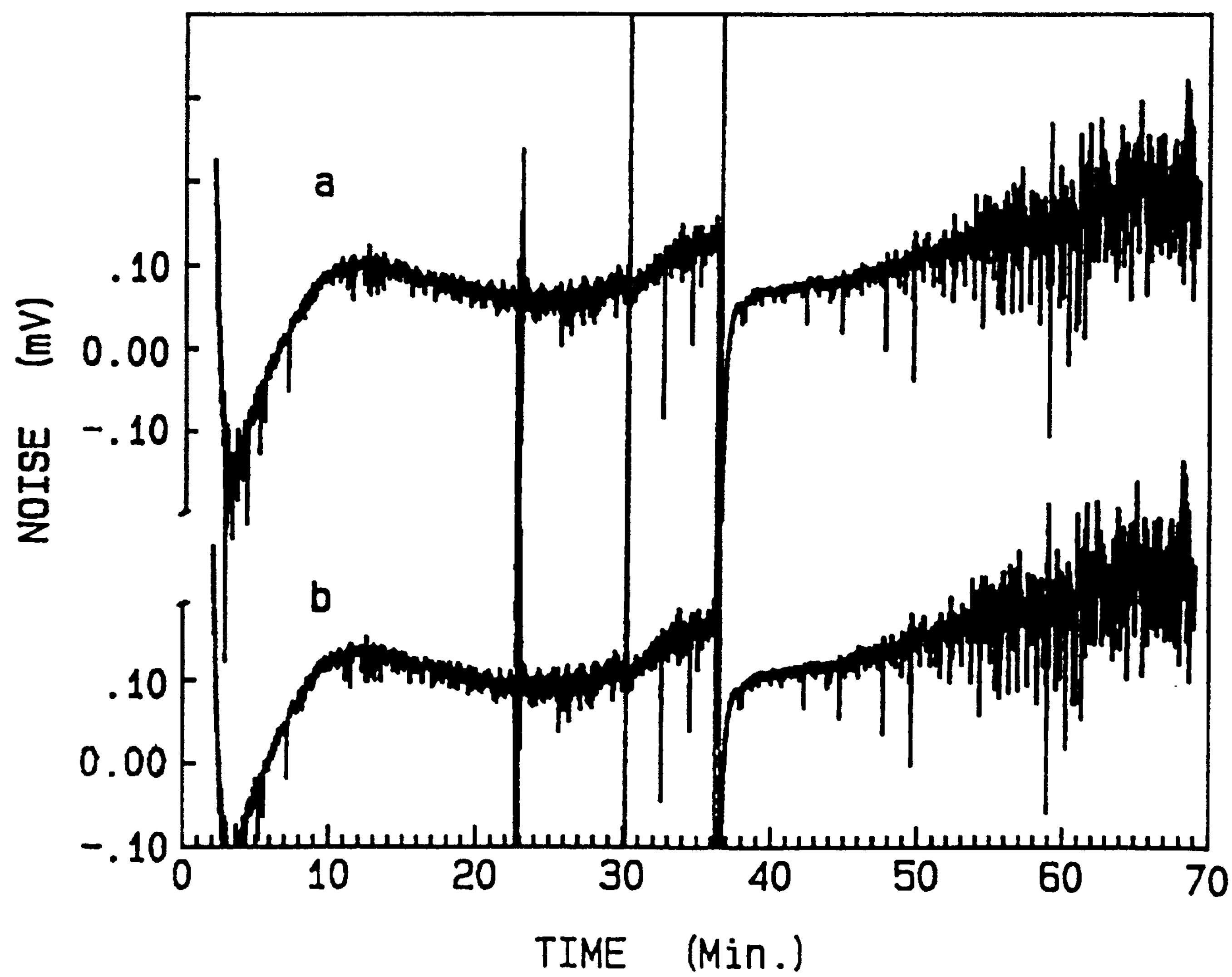
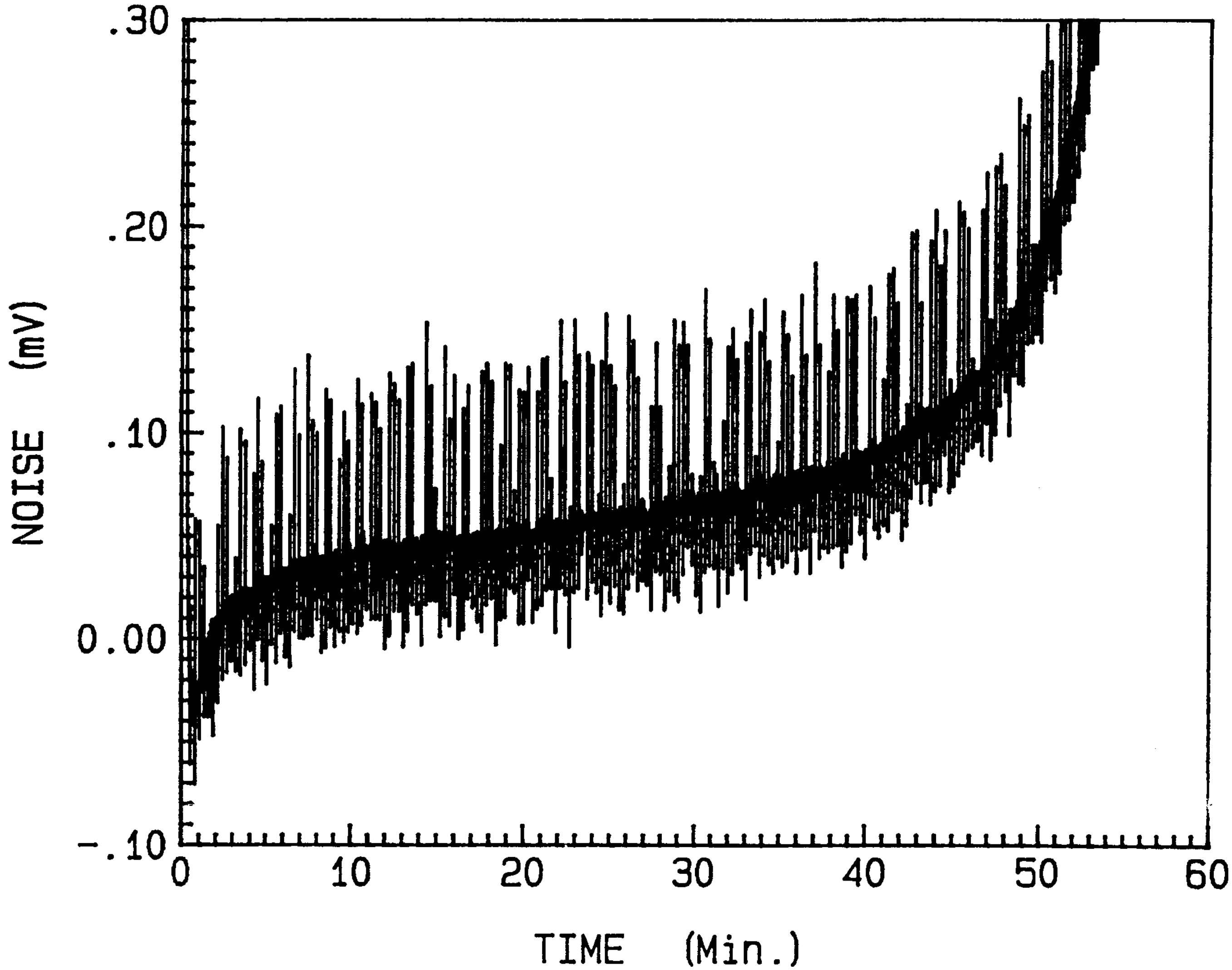


Fig 3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10
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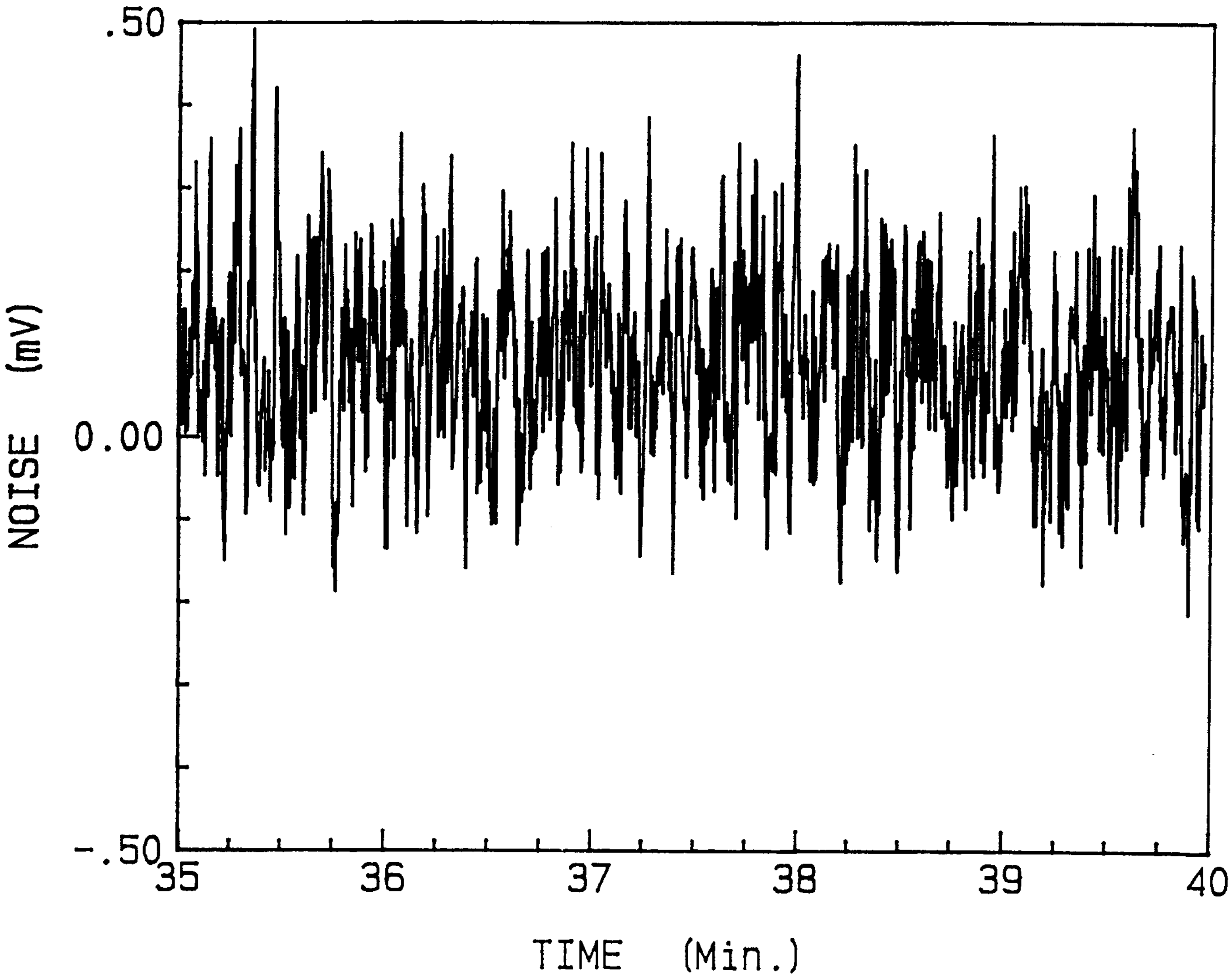
30
40
50
60
TIME (Min.)



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NOISE (mV)
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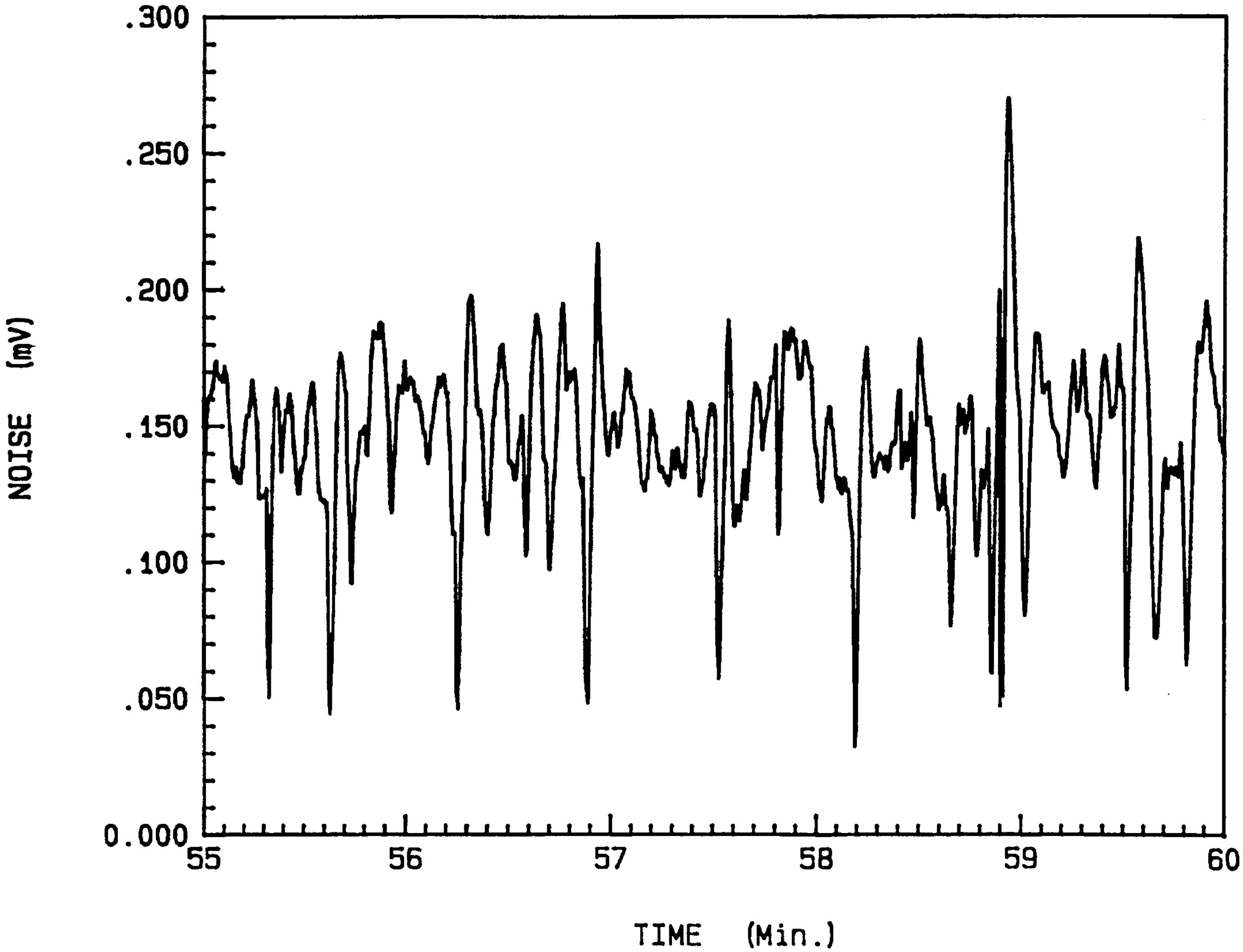
36
37
38
39
40
TIME (Min.)



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NOISE (mV)
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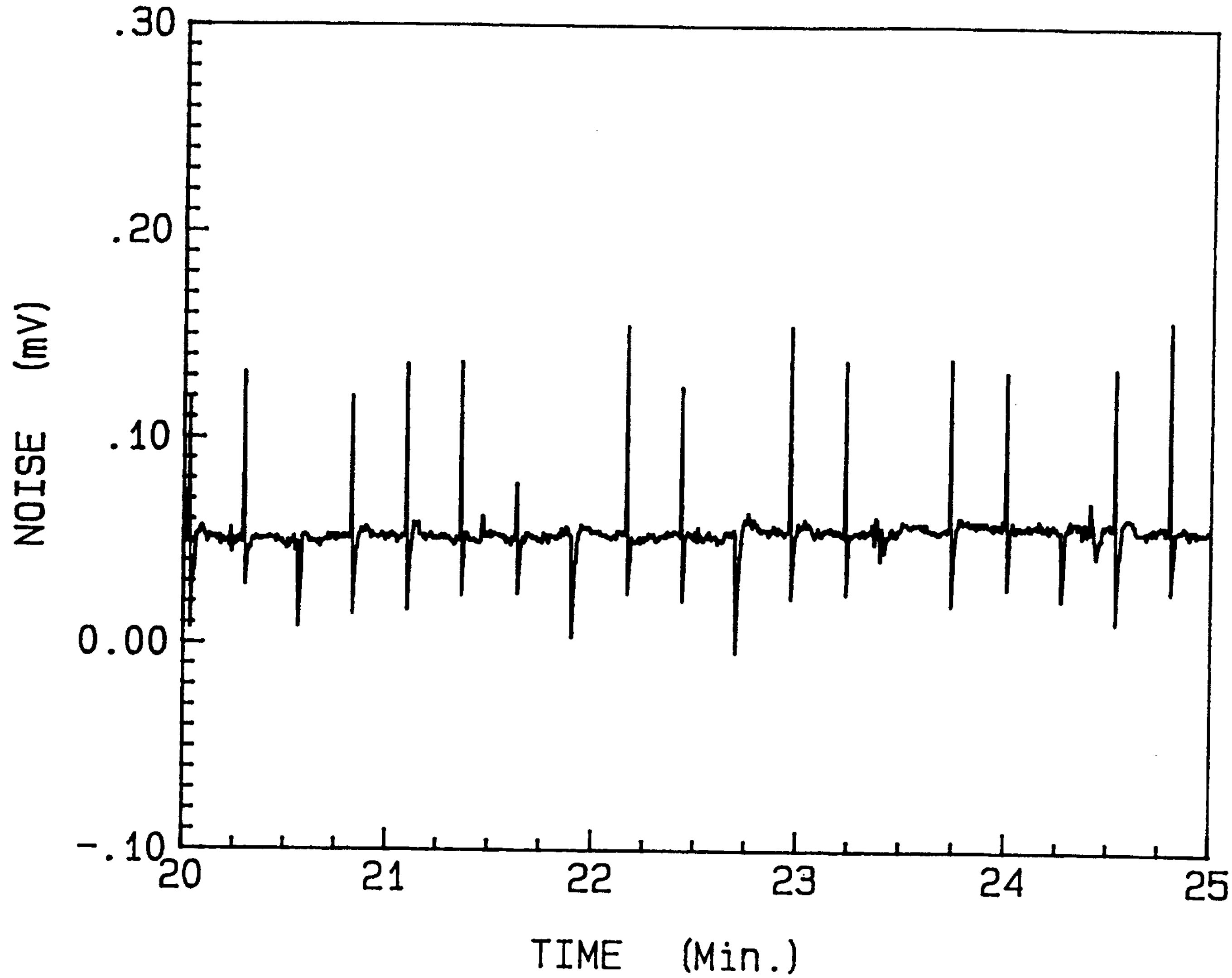
56
57
58
59
60
TIME (Min.)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22
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25
TIME (Min.)