Stability of Iridium Oxide Films in High Temperature, 200-250°C, Solutions

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INTRODUCTION

This report relates to the Interagency Agreement No. 87-08 "Assessment of Metrological Uncertainties for Waste Package Testing" and reports on the experimental program progress through September 30, 1989. Previous reports have included NBSIR 85-3237 "Review of Materials for pH Sensing for Nuclear Waste Containment"[1], the NBSIR 88-379/NUREG-CR-5166 "Electrochemical Evaluation of Solid State pH Sensors for Nuclear Waste Containment"[2], and pH Sensors Based on Iridium Oxide"[3].

The primary goal of this project is to provide improved technology for the fabrication of pH sensing electrodes and characterization of the electrochemical properties of the fluids surrounding nuclear waste packages in the repository. Specifically, the measurement of the pH and Eh of the fluids are of prime concern. A probe has been selected which includes an electrode for measuring these to characterize the electrochemical activity of the fluid surrounding the containment. The approach selected has been to focus on the IrO_2 thin film electrode for electrochemical measurements. IrO_2 has indicated promise of stability at the harsh, high temperature conditions of the repository and in the harsher conditions present in corrosion testing. Other advantages of the IrO_2 films include the rugged nature of the electrode, ease of miniaturization, high voltage/low impedance output, and low cost of fabrication.

The experimental program to date has included an examination of the performance of the IrO_2 pH electrode including long term testing, the reproducibility of the fabrication procedure, and the characterization of its short time response. In addition we have reported on the electrochemical behavior of the pH electrode and the solid surface characterization of the electrode to determine the mechanisms of its functional behavior and to lay the basis for improving the electrode.[3,4]

The results so far in this program indicate IrO_2 thin film sensors could be used at temperatures up to 200°C which exceeds the upper operating limit of the glass electrode. Other advantages of ruggedness, simplicity, size, and insensitivity to alkali ions also indicate the validity of the approach. In order to take advantage of this capability, we have developed bonding techniques to improve the physical stability of the film-substrate structure. This was reported earlier this year. However, drift problems with the IrO_2 would require calibration before each use and we are attempting to find ways to alleviate these effects. Our other area for major emphasis is to document the high temperature performance of the IrO_2 films and their substrates.

EXPERIMENTAL PROCEDURE

In this report, we shall discuss the results of our high temperature acidic and alkaline exposure of the IrO_2 films on $A\ell_2O_3$ substrates. These tests include a measurement of electrode potential versus a single junction Ag/AgCl reference electrode (+0.175 vs NHE) and a comparison to the pH as measured with a standard glass electrode. The electrochemical tests were performed in a stirred, air saturated, buffer solution (294-296°K) consisting of 0.01M acetic, phosphoric, and boric acids and 0.1M potassium nitrate.[6] Titration was performed by first adding sodium hydroxide to the pH 2.1-2.3

buffer solution followed by nitric acid additions to lower the pH (FIG 1-43 and Tables 1-5). High temperature exposure was made in a 125cc teflon lined bomb using potassium hydrogen phthalate (pH 4.01), disodium hydrogen phosphate-potassium dihydrogen phosphate (pH 7), sodium hydrogen carbonate-sodium carbonate (pH 10.01) and deionized water as test solutions for the iridium oxide. The bomb was heated in a standard laboratory box furnace and the temperature was controlled $\pm 5°C$.

The plan of testing was to compare the electrochemical potential of the films before and after exposure to deionized water, pH 4, 7, and 10 at 200°C (15.5 bar or 225 psi) and 250°C (40 bar or 600 psi); actually the higher temperature was 245° $\pm$ 5°C. This was accomplished simply by placing the bomb containing the solutions and electrodes in a temperature controlled furnace for 20 (or 70) hours. Fresh specimens were used for each pH exposure at 200°C. Four depositions designated I50, I52, I53, and I54 were used as sources for the samples. Each deposition was made on $A\ell_2O_3$ circuit board at 30-40°C or 250°C, in 50% Ar-O_2 mixtures (0.4 Pa) by DC magnetron sputtering of a 99.99% Ir target. Film thicknesses were approximately 1 μm. The sample series designated I50 was deposited on $A\ell_2O_3$ at 250°C which leads to a crystalline deposit[5] whereas deposition at room temperature leads to an amorphous deposit. The only intentional difference between the room temperature depositions pertained to the substrate preparation which was not expected to affect the electrochemical properties. I52 had solvent plus UV ozone treatment, I53 had ion beam cleaning and ion beam assisted initialization of the deposit to improve the bonding, and I54 had a thin (60 nm) Cr-Cr_xO_y bond coat to improve the $A\ell_2O_3$-IrO_2 adhesion.

RESULTS

The results of these tests are presented in FIG 1-53. The format includes labelling the deposition, plotting potential difference in volts versus pH, the slope (Nernstian) and intercept (Eo), and the sample number (A1-6) from each deposition. The title of each graph gives the condition (i.e. fresh, 200°C, 20 or 70 hours) and the pH of the solution at room temperature. When no time is indicated, the exposure was 20 hours. Each sample was started at a pH near 2 and was titrated with NaOH to a pH near 10. This was followed by titrating with HNO_3. The decreasing pH return is designated "d". Thus the information contained in the figures indicates the variation from sample to sample on each deposition, variations between depositions made under similar conditions, and degradations due to the high temperature exposure.

The test coupons A1 (FIG 1-13) include results of tests after exposures at 200°C, 20 hours, of pH 4, 7, and 10 subsequently and a final "bake out" exposure to oxygen at 500°C. Generally the high temperature aqueous exposure did not systematically change the slope, although the slope for all coupons was lower after the pH 7 exposure and higher after the oxygen 500°C exposure. The A2 series included only exposure to deionized water at room temperature of 24, 500, and 1400 hours (FIG 14-23). No consistent pattern emerges and the spread in values of the slope is similar to that between depositions and between samples on a given run.

The sample series A3 (FIG 24-31) was used to investigate the exposure in a buffered pH 7 solution at 200°C for 20 and 70 hours. Although the 20 hour exposure did not affect the electrochemical behavior it would appear that

after 70 hours some significant decrease in slope may have occurred. This solution contains Na_2HPO_4 and KH_2PO_4 which may react with the IrO_2 at 200°C.

The A4 series (FIG 32-39) was used to investigate reactions at 200°C and 240°C in pH 10. Although no degradation was evident at 200°C a decrease in the slope is apparent at 240°C (FIG 38-39). Samples A5 (FIG 40-42) were exposed to pH 7 at 250°C and the films came off the $A\ell_2O_3$ as a powder. The "fresh" results are given to add to the data base for reproducibility. A6 samples (FIG 43) were exposed to deionized water at 250°C and a similar loss of the film was observed.

The sample series I50 was deposited at 250°C and therefore the iridium oxide has the rutile crystal structure.[5] The results before and after exposure in the pressurized bomb at 200°C are presented in FIG 44-53. Figures 45, 47, and 49 are test results after an overnight soak at pH 2.23 at room temperature. Although the slope is unaffected in each case the formal potential, Eo, is significantly diminished. These results agree with those previously reported.[4] After 20 hours at pH 4 (FIG 50), little change in slope or intercept is observed. FIG 51 and 52 report the results after 20 and 40 hours at 200C in pH 7, again it appears the film is not degraded. FIG 53 shows the results of exposure to pH 10 for 20 hours, in this case the return (decreasing pH titration) slope was lost when the solution shorted to the connecting clip and no observation of the hysteresis could be made. The behavior of the crystalline films appear to be similar to the amorphous films which were deposited at room temperature.

SUMMARY

We have examined the sensitivity of iridium oxide thin films on alumina substrates to high temperature (200, 240°C), high pressure (up to 40 bar, 600 psi) acidic, and basic solutions. Twenty-one sample coupons were electrochemically tested through titrations (pH 2-11) before and after several exposures. Under the most severe conditions at pH 7 and below and at 250°C the film is lost from the $A\ell_2O_3$. This may be a substrate or a film problem; we also observed that the films were less stable on silicon wafer substrates. The electrode potential response was not strongly affected by exposures of 20 hours at pH 4, 7, or 10 at 200°C. However, both the pre-exponential factor and the potential pH slope appeared to drop after 70 hours (200°C) at pH 7 in Na_2HPO_4 and KH_2PO_4. No clear differences were observed between the amorphous and crystalline films. It should be also noted that the scatter in the data for the electrochemical potential was a problem compared to a glass electrode. We are planning a major portion of our effort in the next quarter to improve this condition and will start testing in simulated "TUFF" solution environments.

REFERENCES

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2. Huang, P. H. and K. G. Kreider, "Electrochemical Evaluation of Solid State pH Sensors for Nuclear Waste Containment", NUREG/CR 5166, National Institute of Standards and Technology, Gaithersburg, MD 20899, July 1988.
3. Tarlov, M. J., K. G. Kreider, S. Semancik and P. Huang, "pH Sensors Based on Iridium Oxide" to be published as NUREG.
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5. Kreider, K. G., J. Vac. Sci. Technol, A4(3) (1986) 606.
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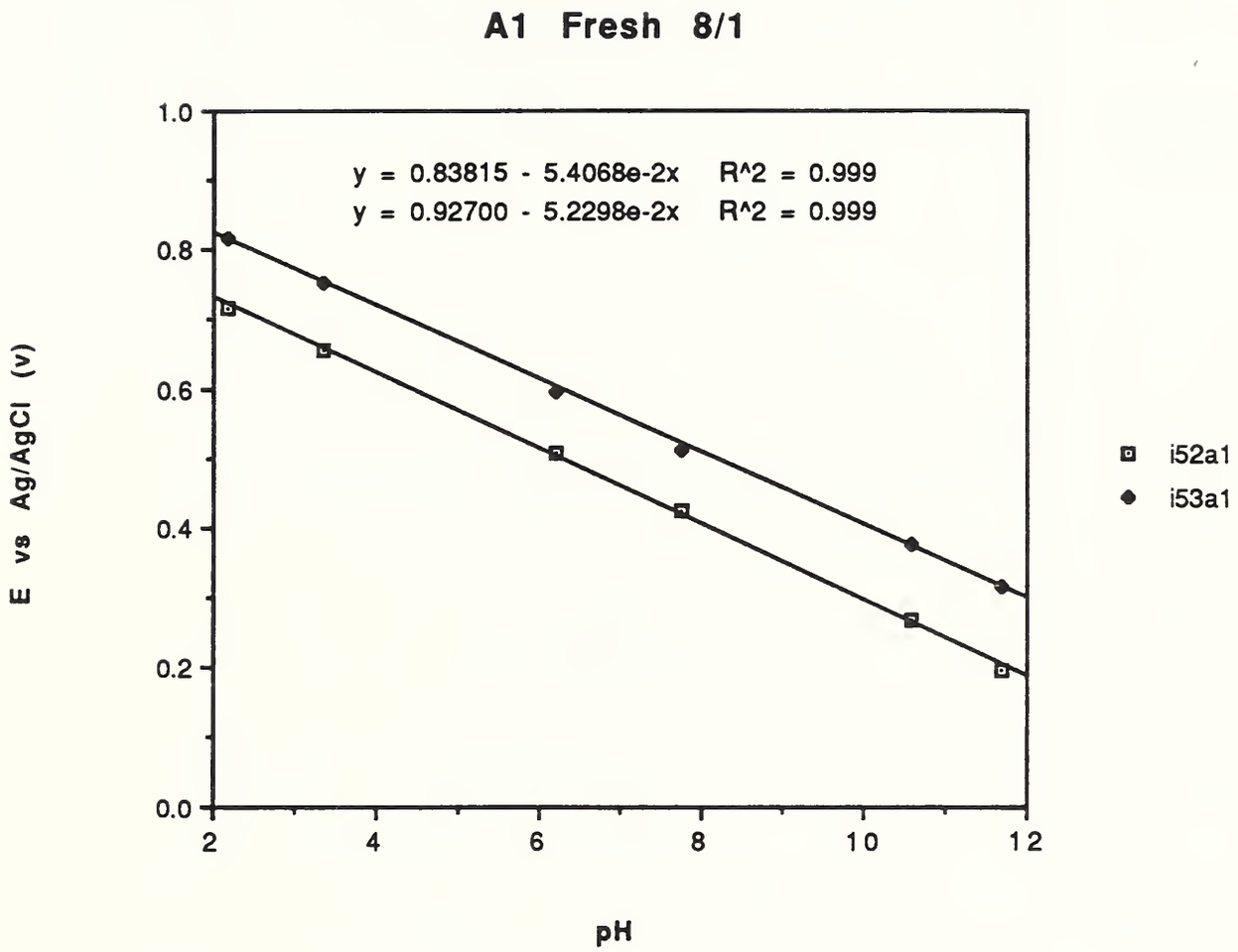
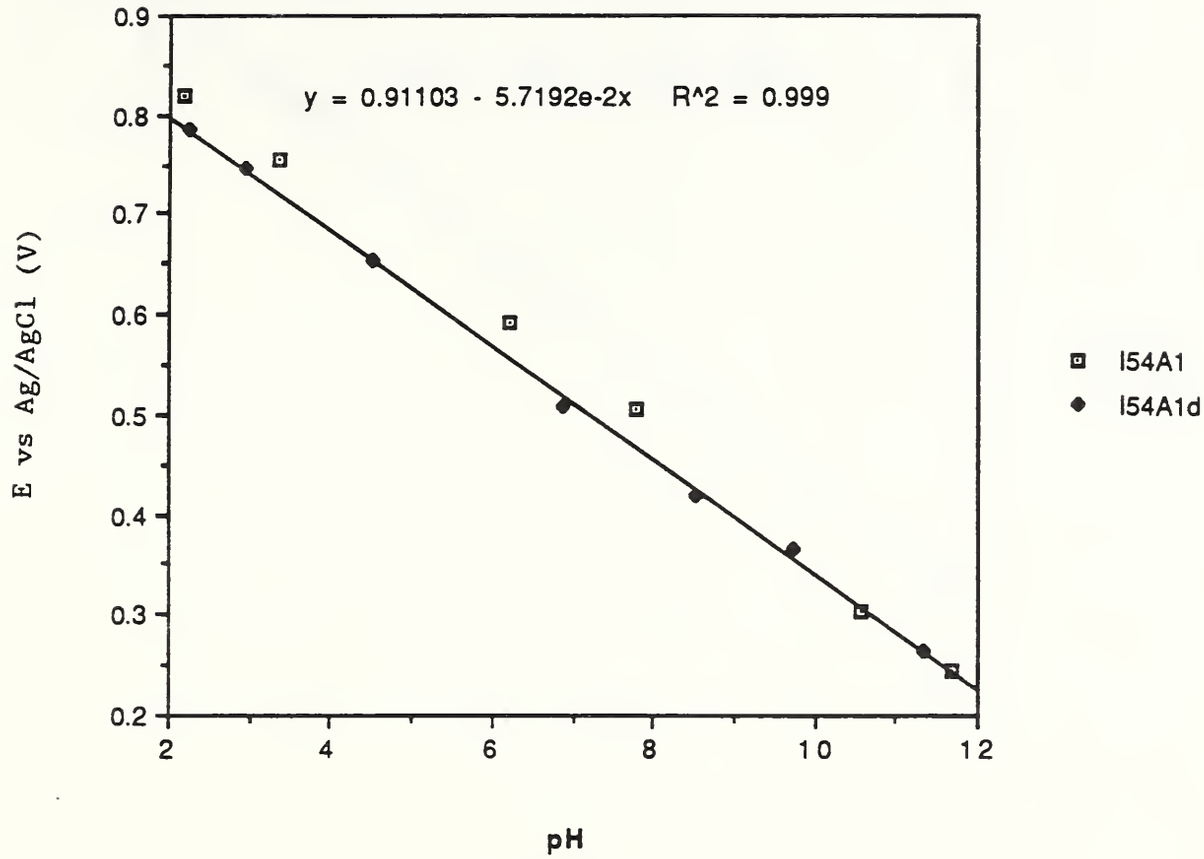
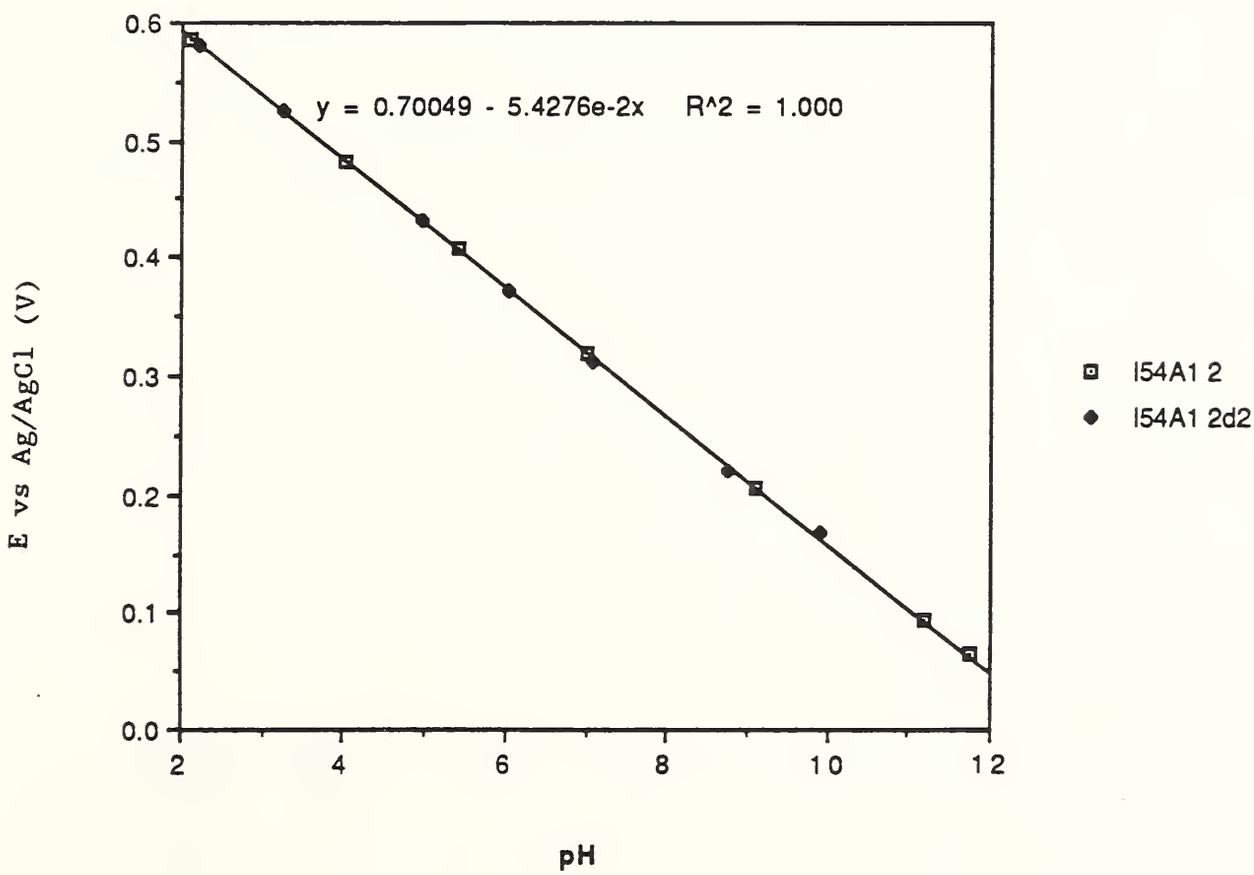

A1 Fresh 8/1
y = 0.83815 - 5.4068e-2x R^2 = 0.999
y = 0.92700 - 5.2298e-2x R^2 = 0.999
1.0
0.8
0.6
0.4
0.2
0.0
2
4
6
8
10
12
E vs Ag/AgCl (v)
pH
i52a1
i53a1

Figure 1

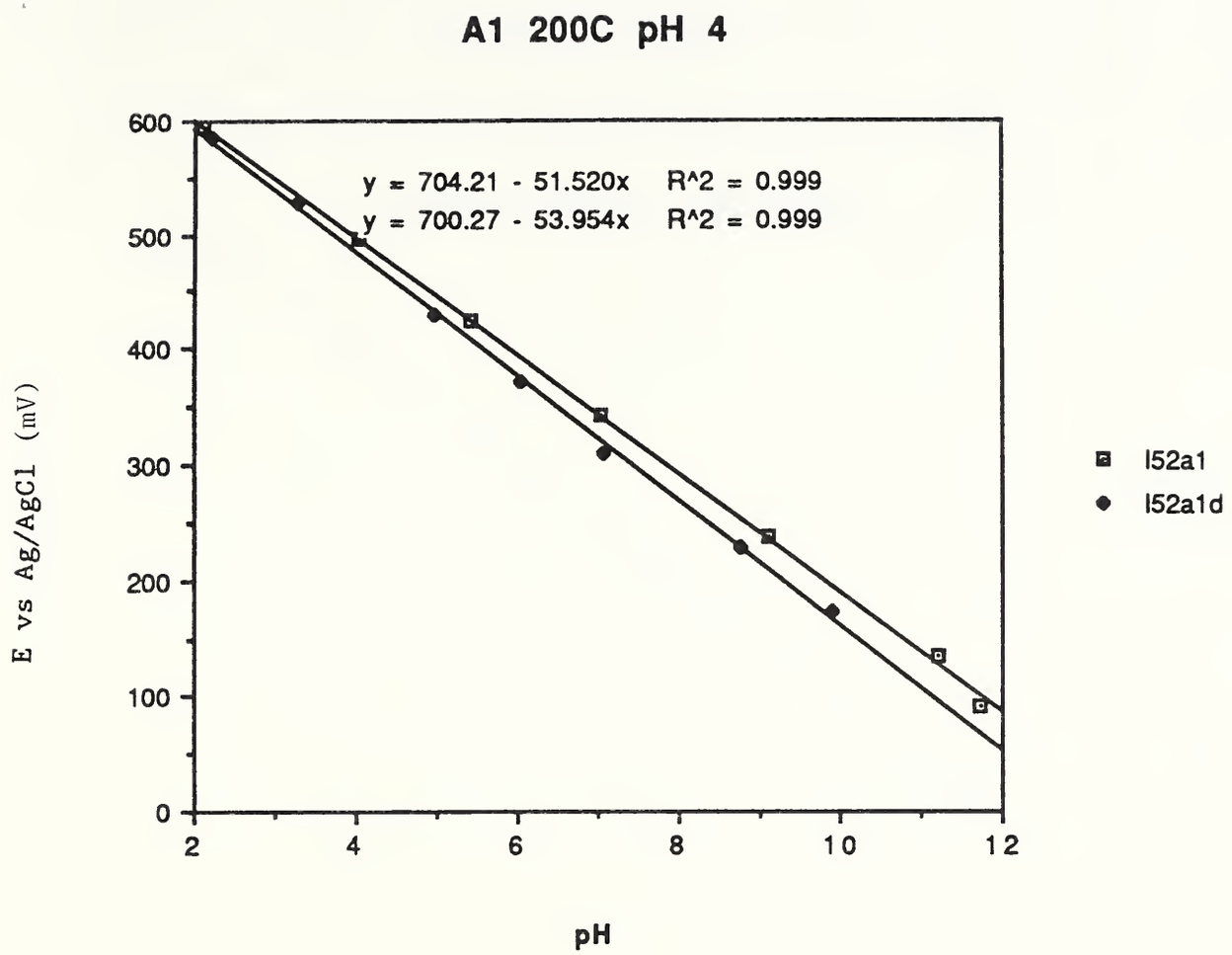
A1 Fresh 8/1

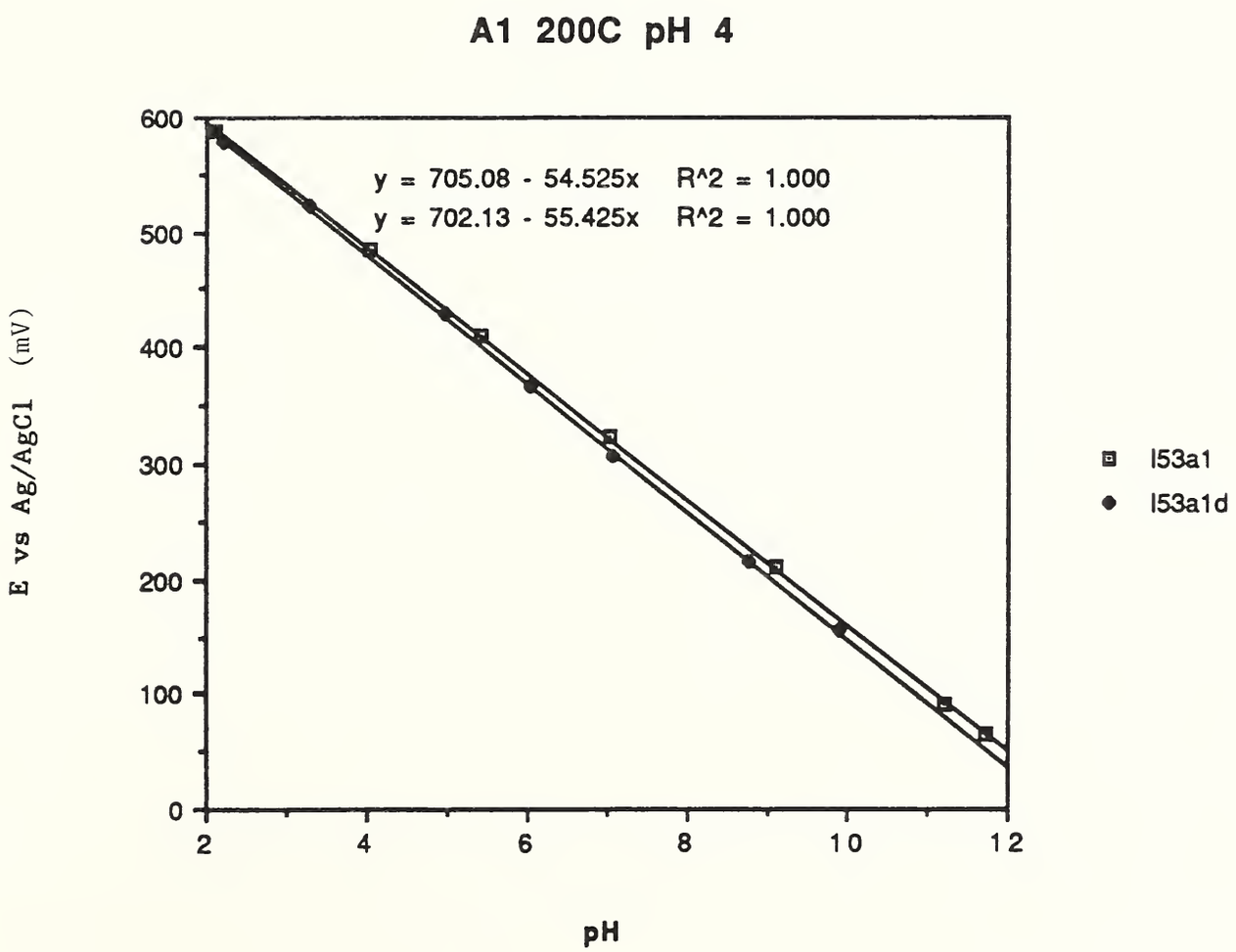


A1 200C pH 4



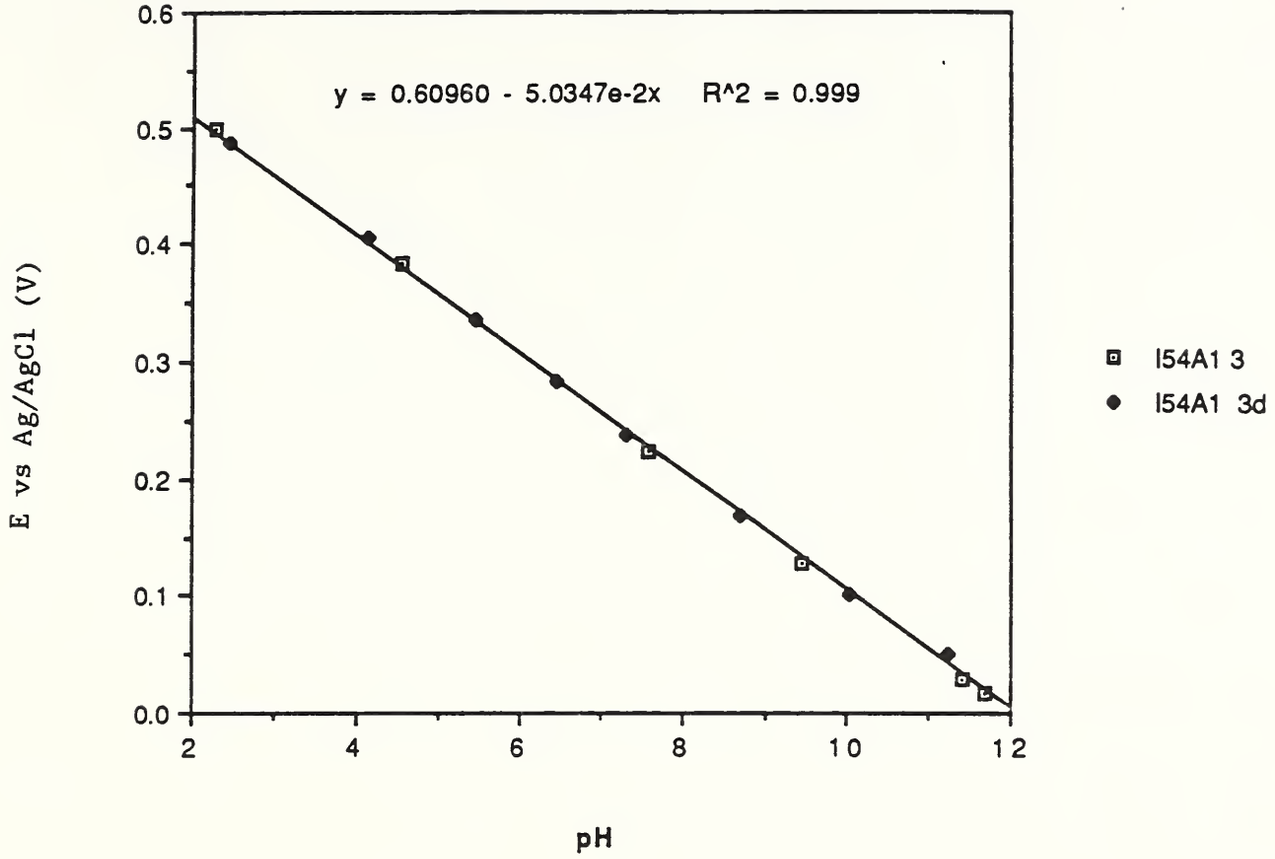
Figures 2-3


A1 200C pH 4
y = 704.21 - 51.520x R^2 = 0.999
y = 700.27 - 53.954x R^2 = 0.999
E vs Ag/AgCl (mV)
pH
I52a1
I52a1d

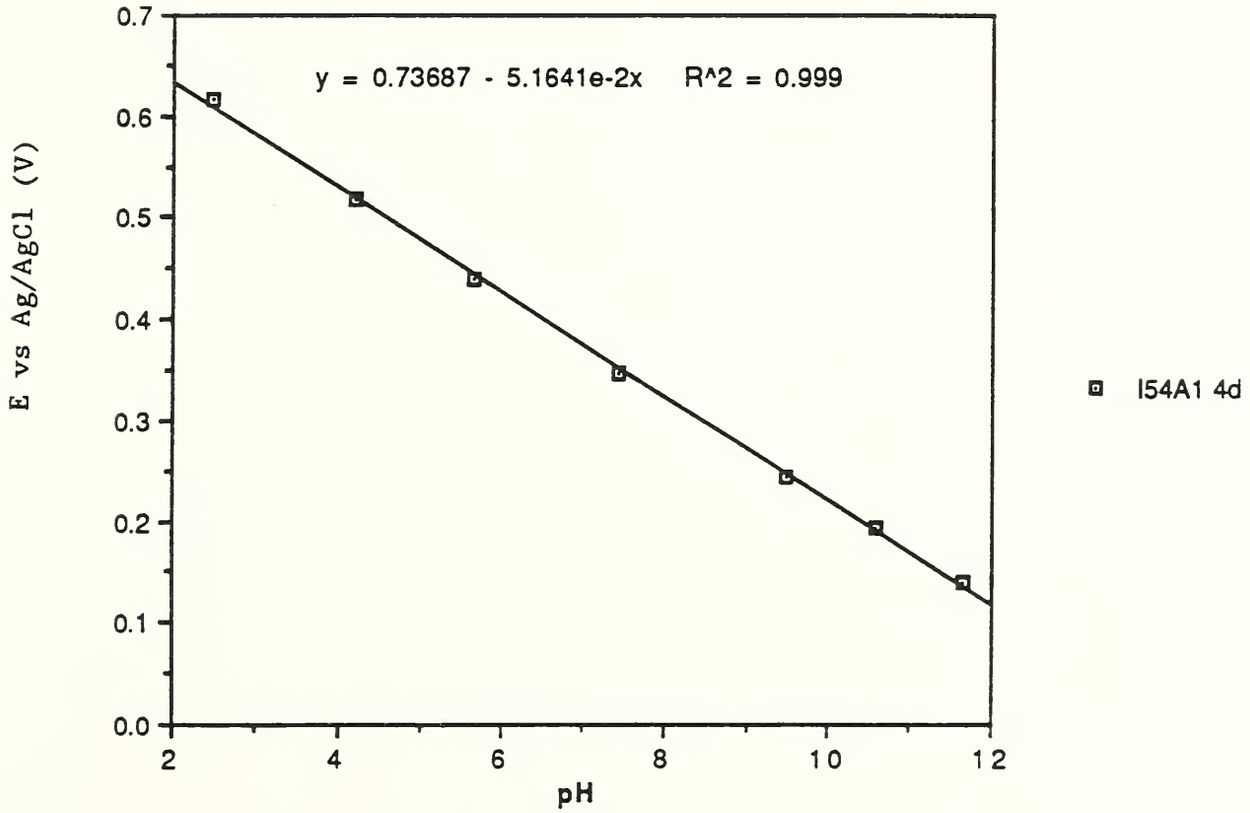

A1 200C pH 4
y = 705.08 - 54.525x R^2 = 1.000
y = 702.13 - 55.425x R^2 = 1.000
E vs Ag/AgCl (mV)
pH
I53a1
I53a1d

Figures 4-5

A1 200C pH 4,7

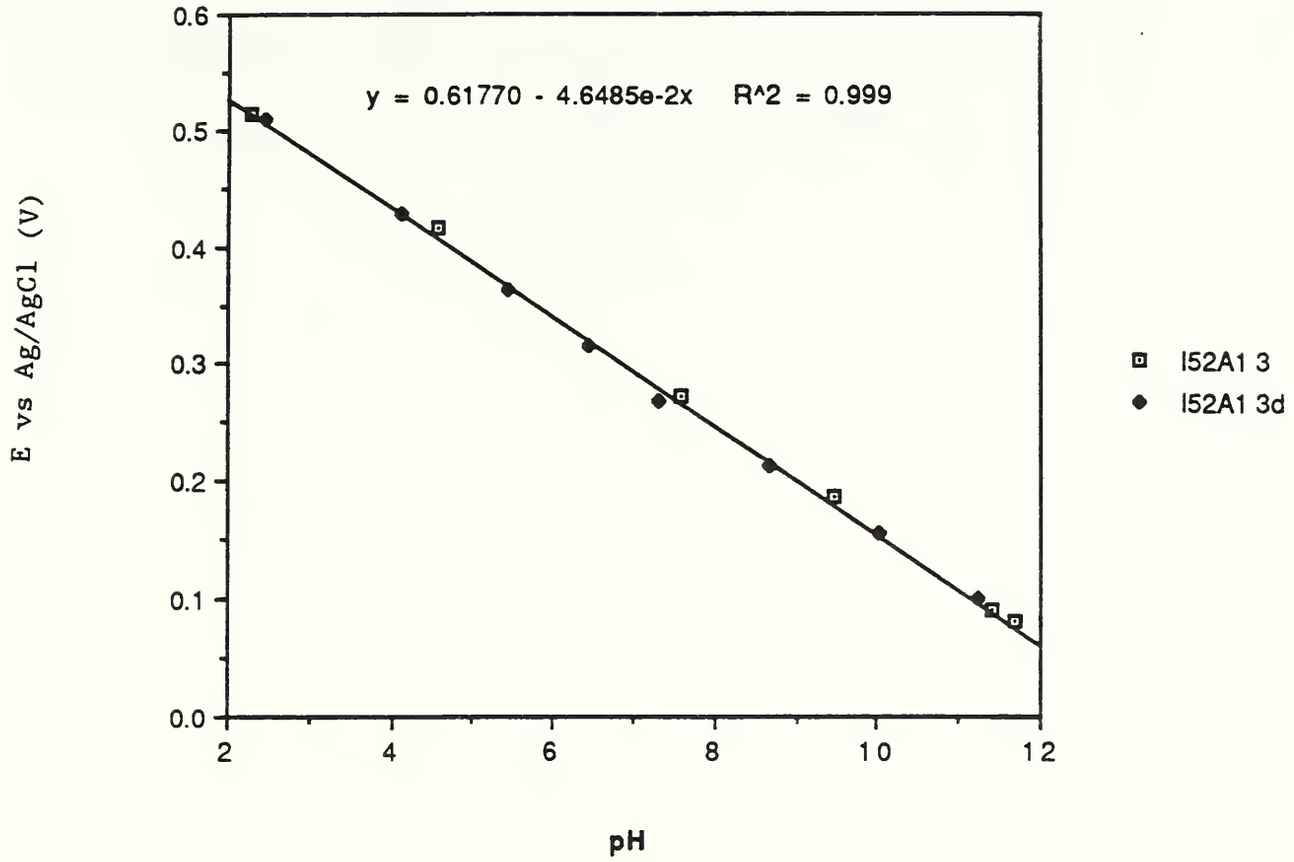


A1 200C pH 4,7,10

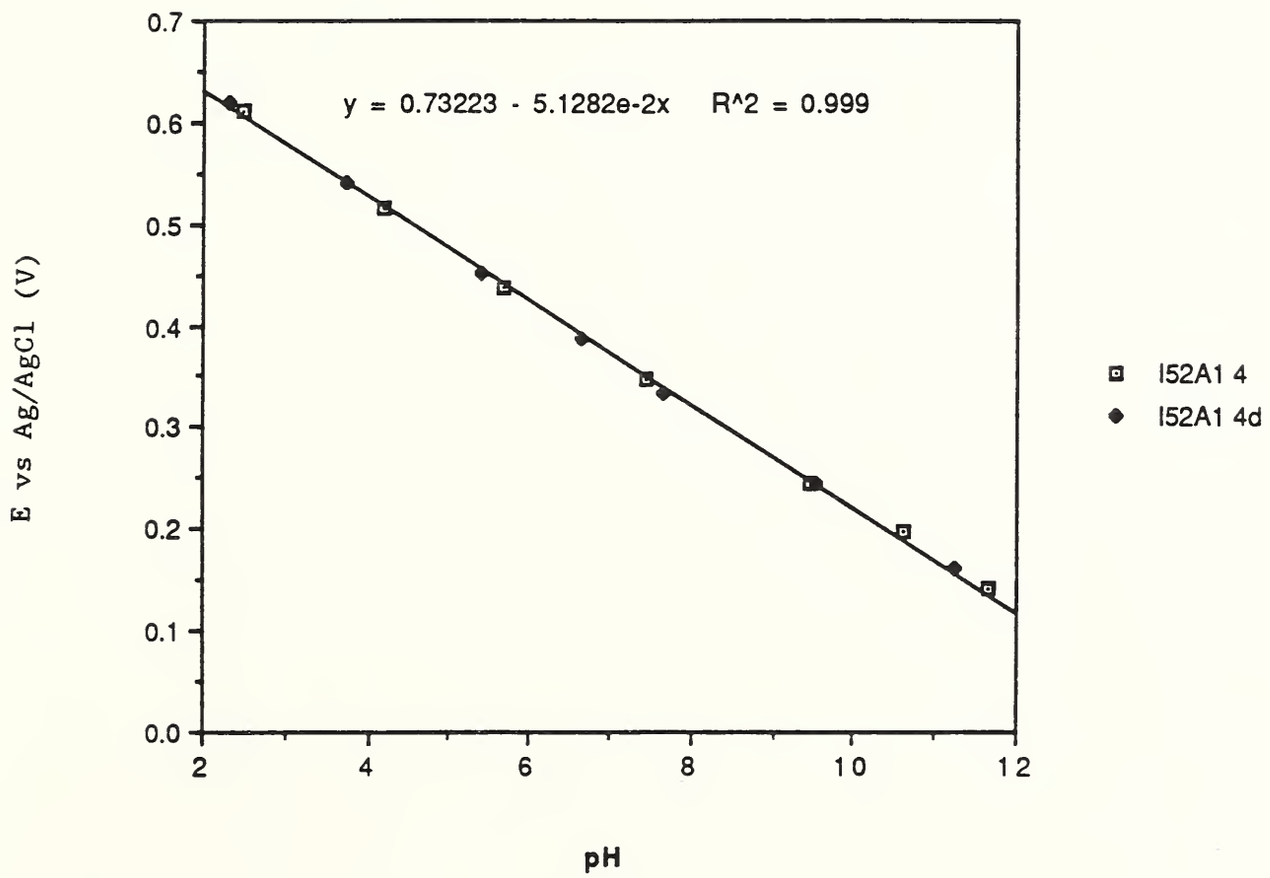


Figures 6-7

A1 200C pH 4,7

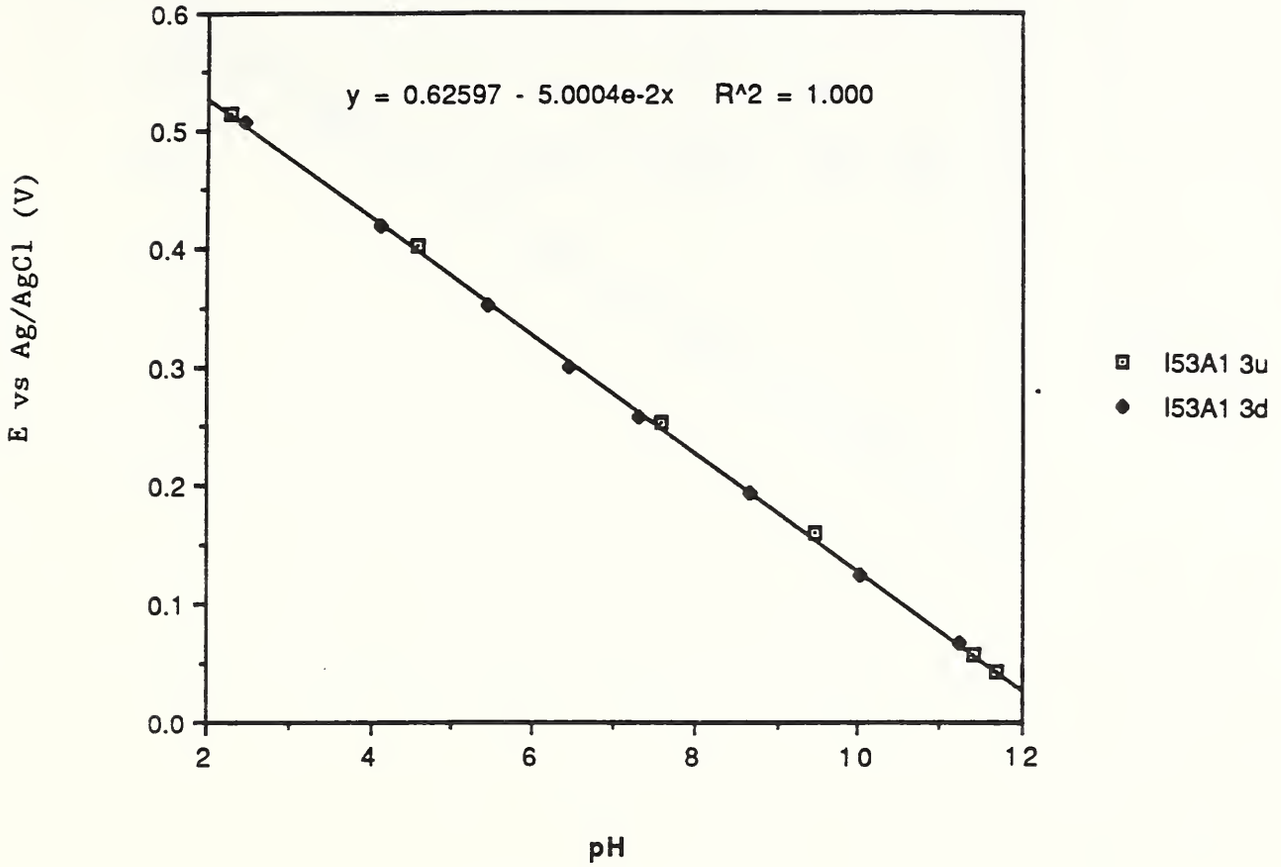


A1 200C pH 4,7,10

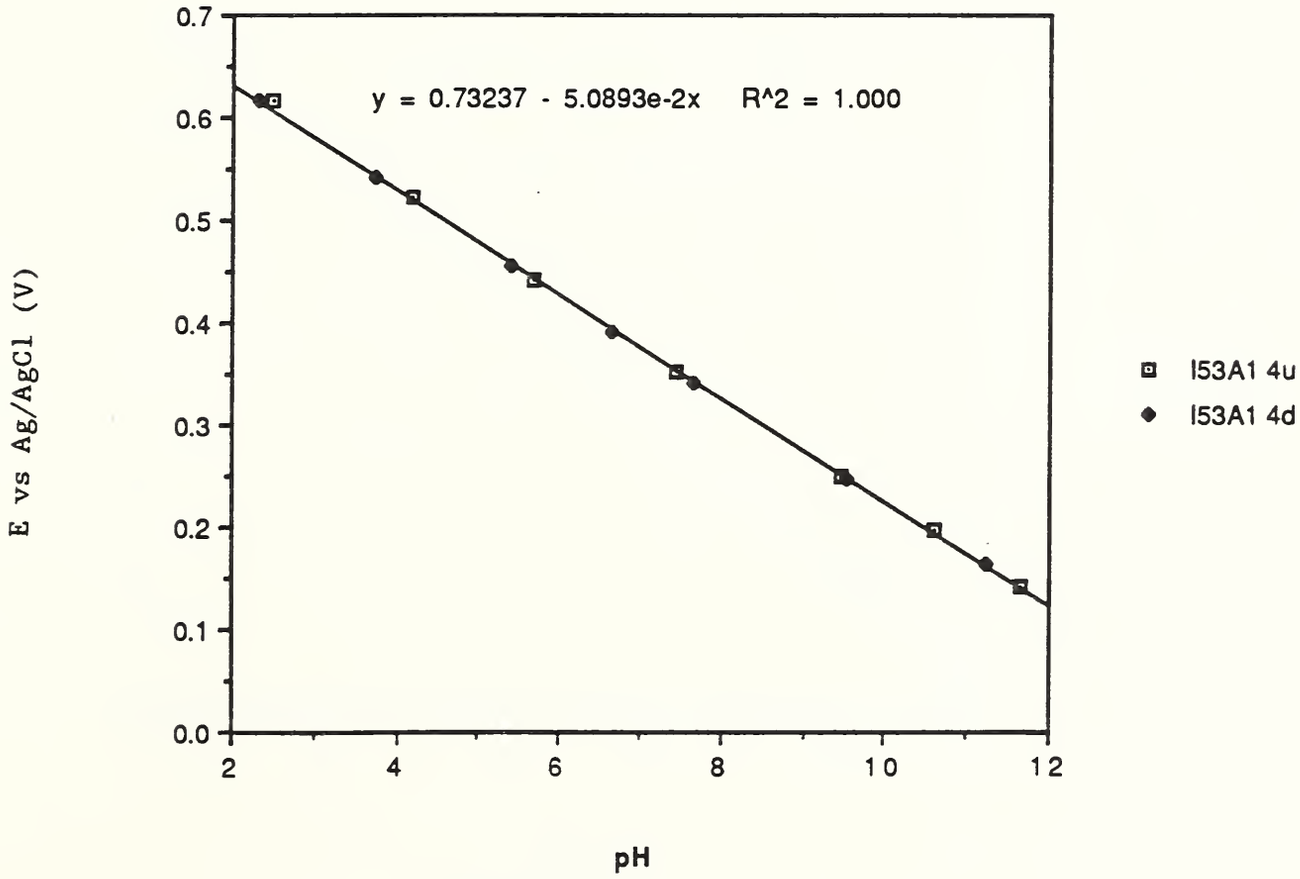


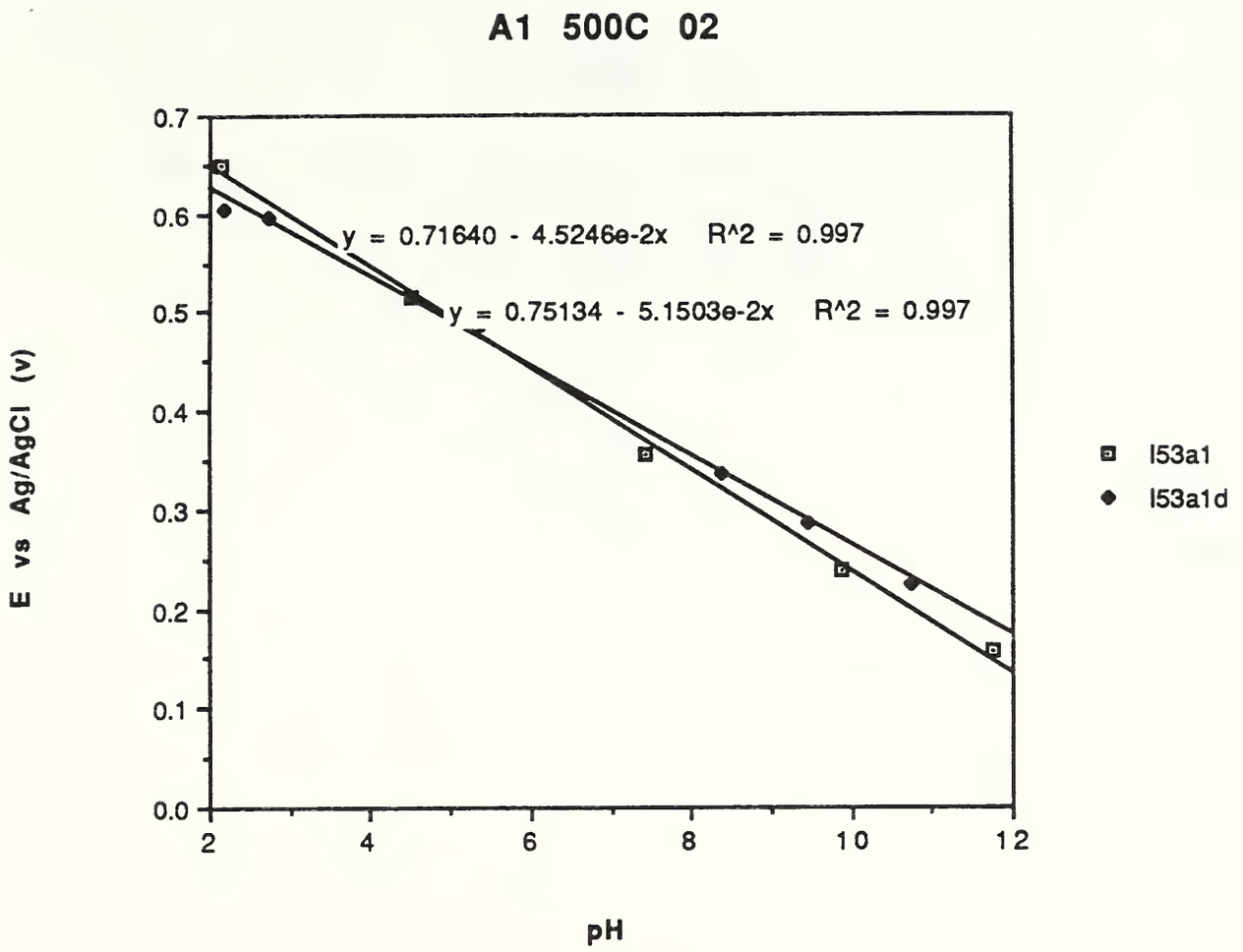
Figures 8-9

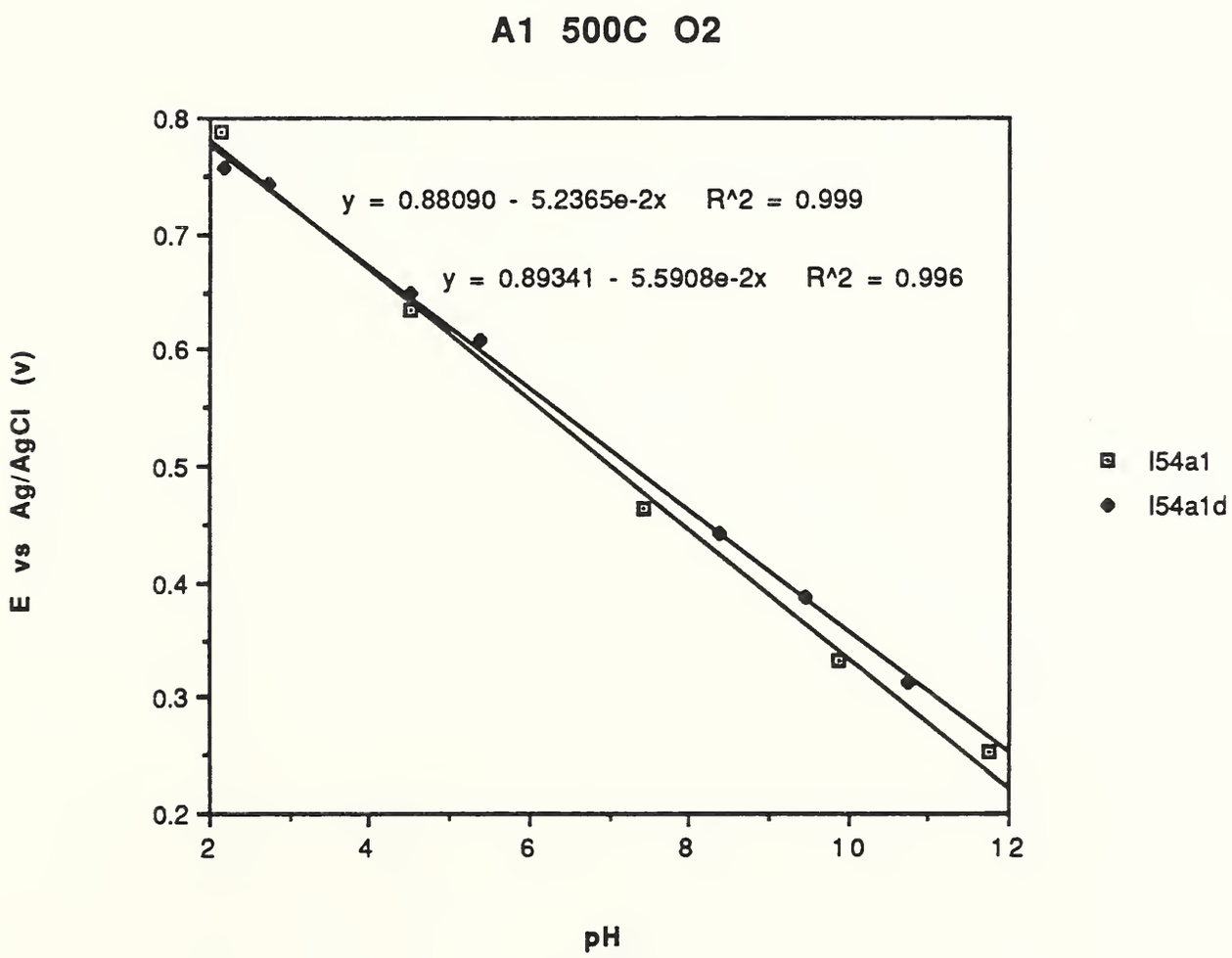
A1 200C pH 4,7



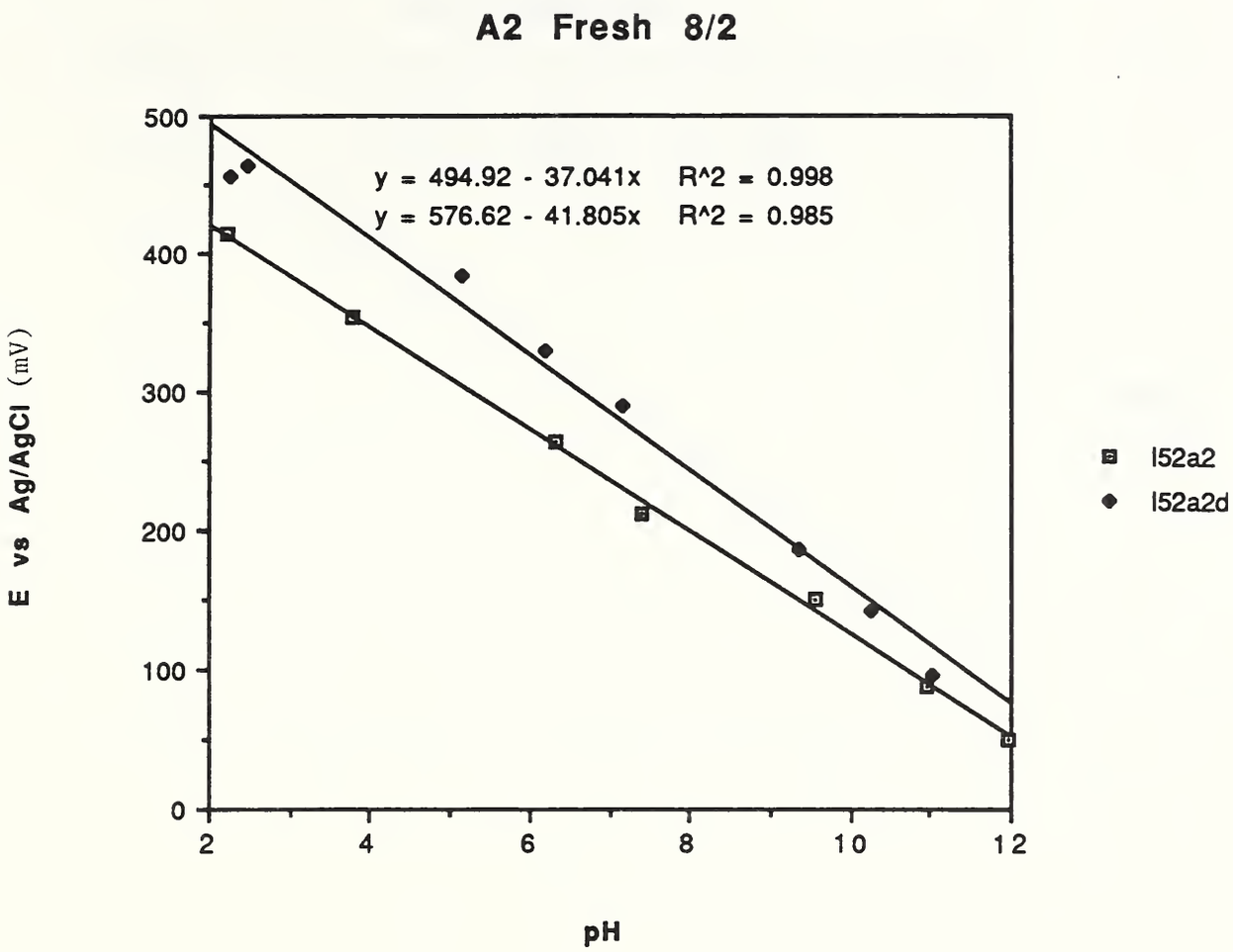
A1 200C pH 4,7,10

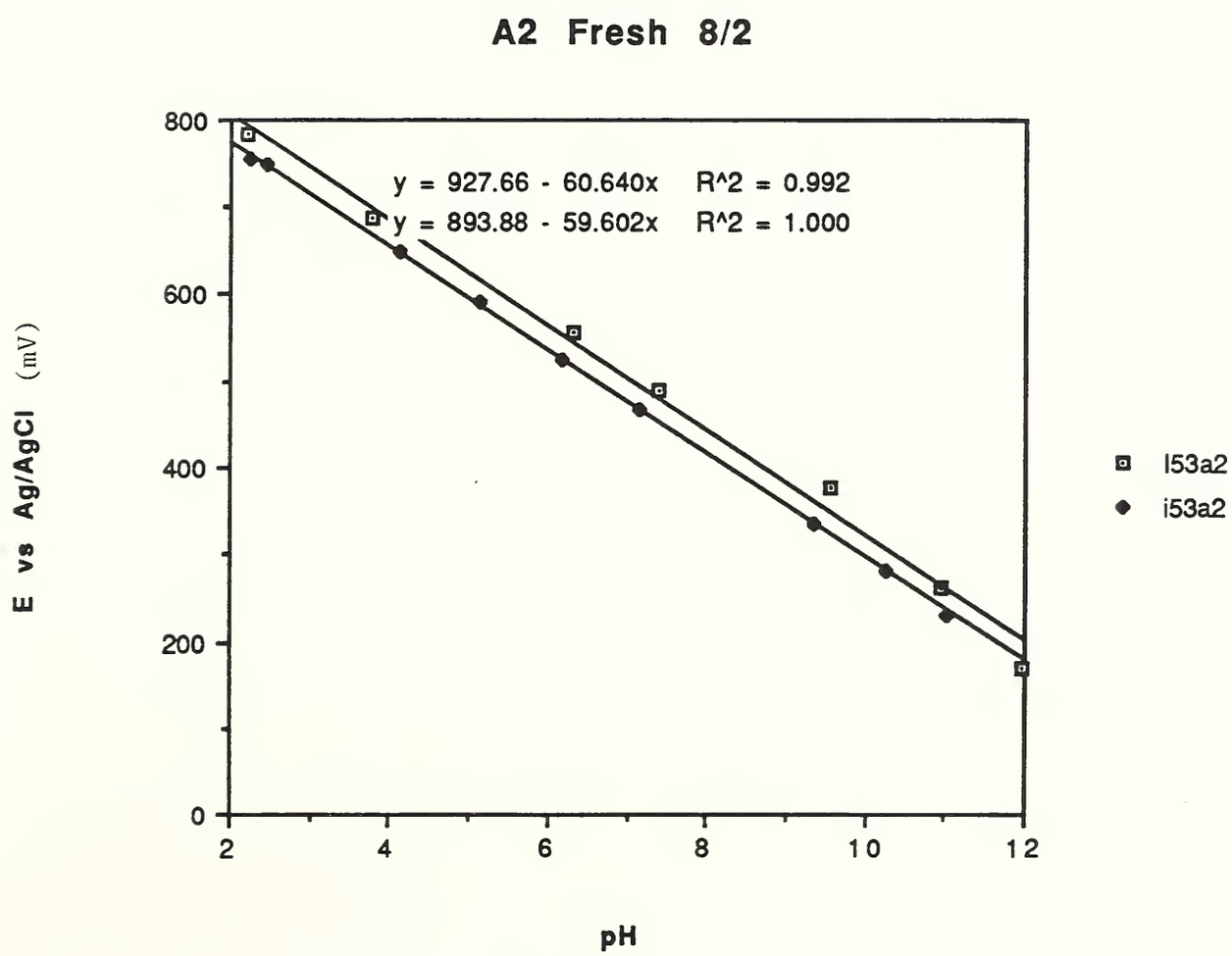






Figures 12-13





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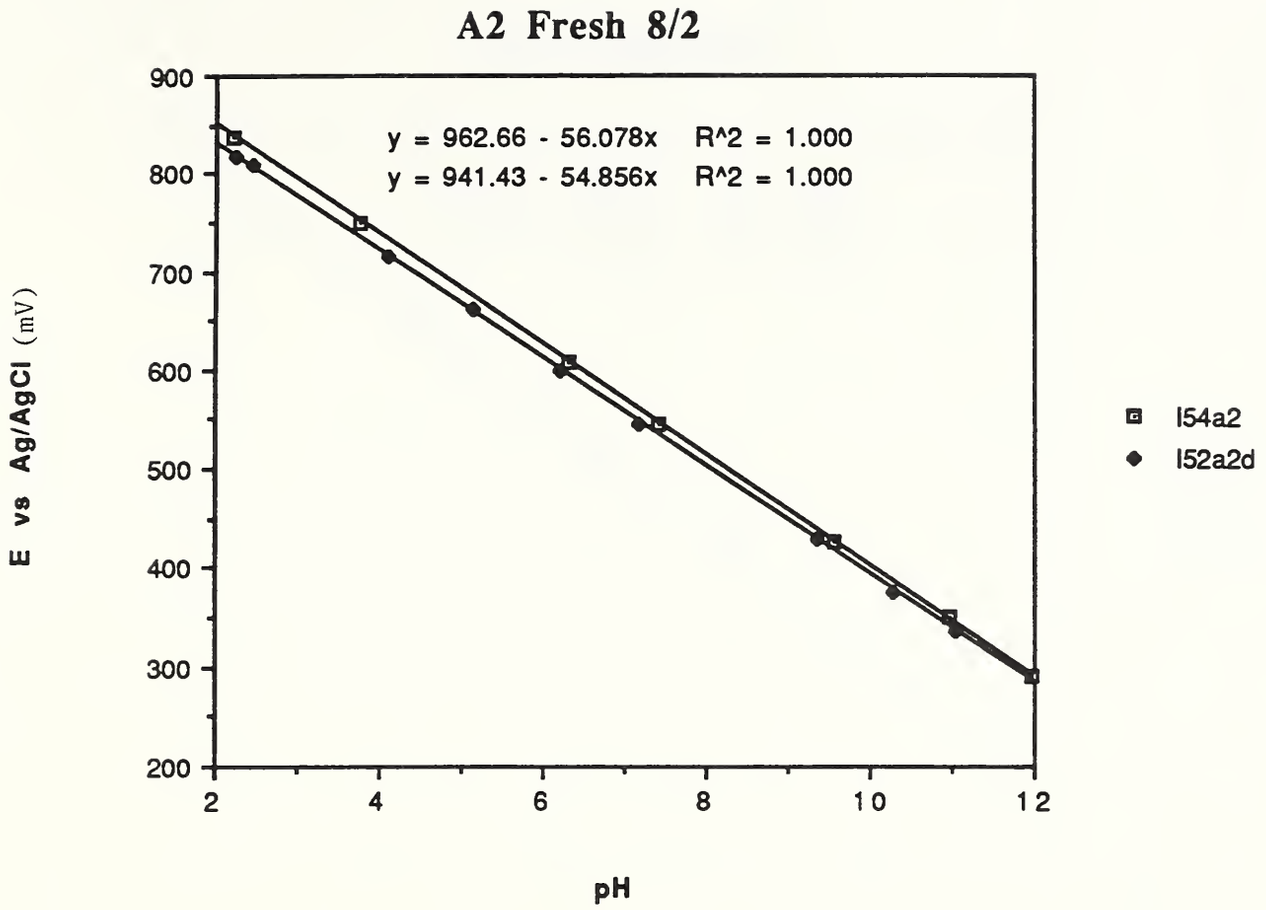

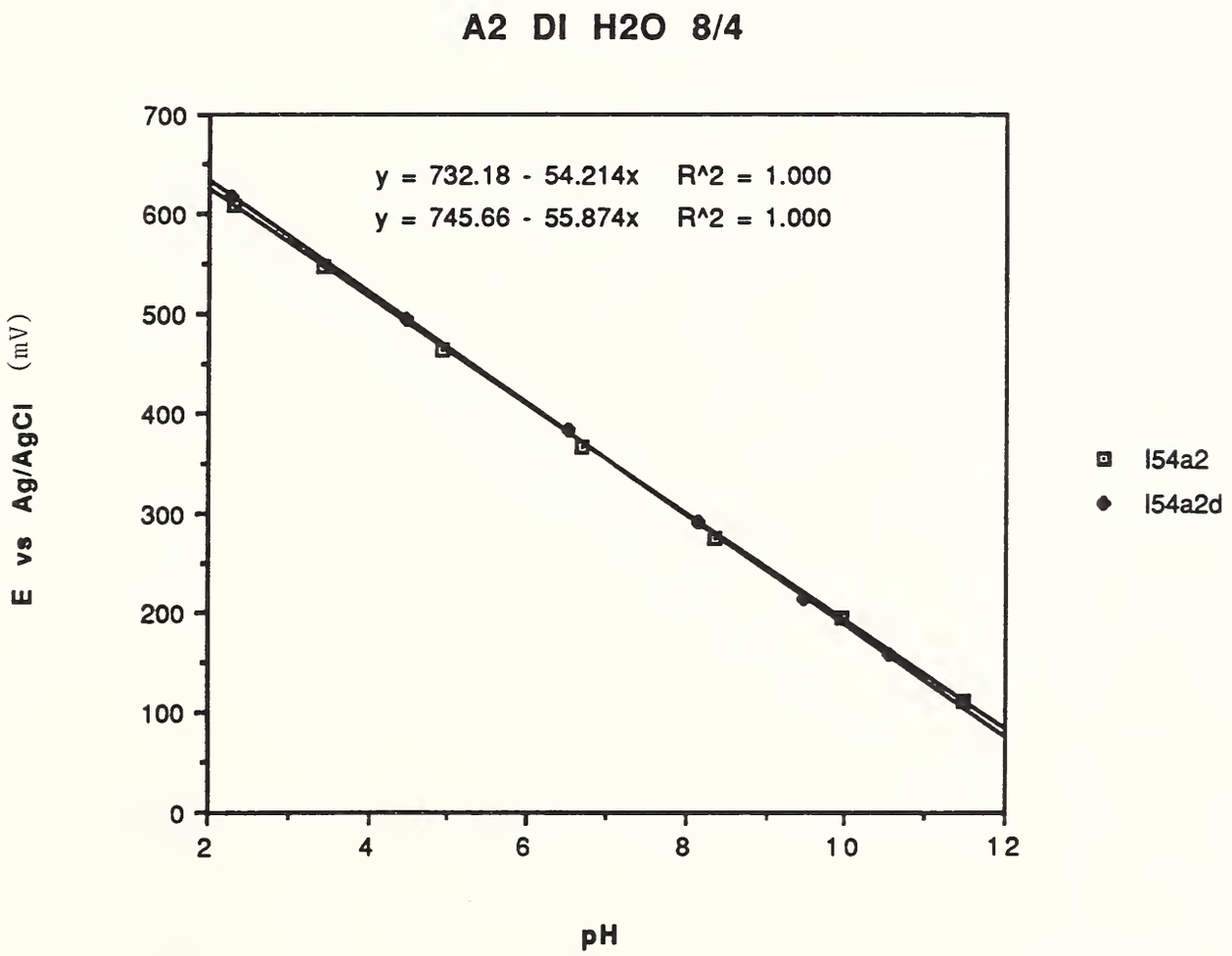

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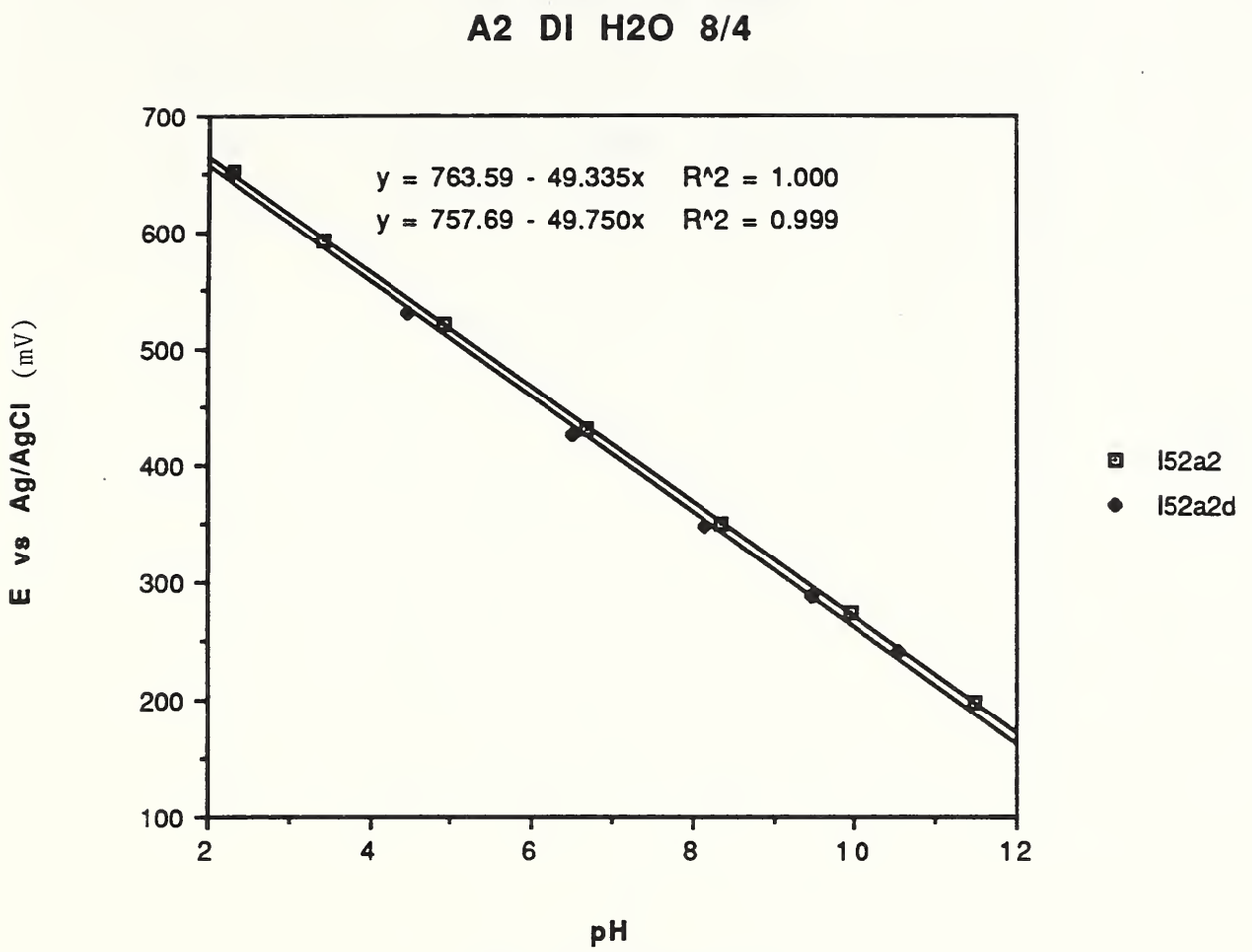

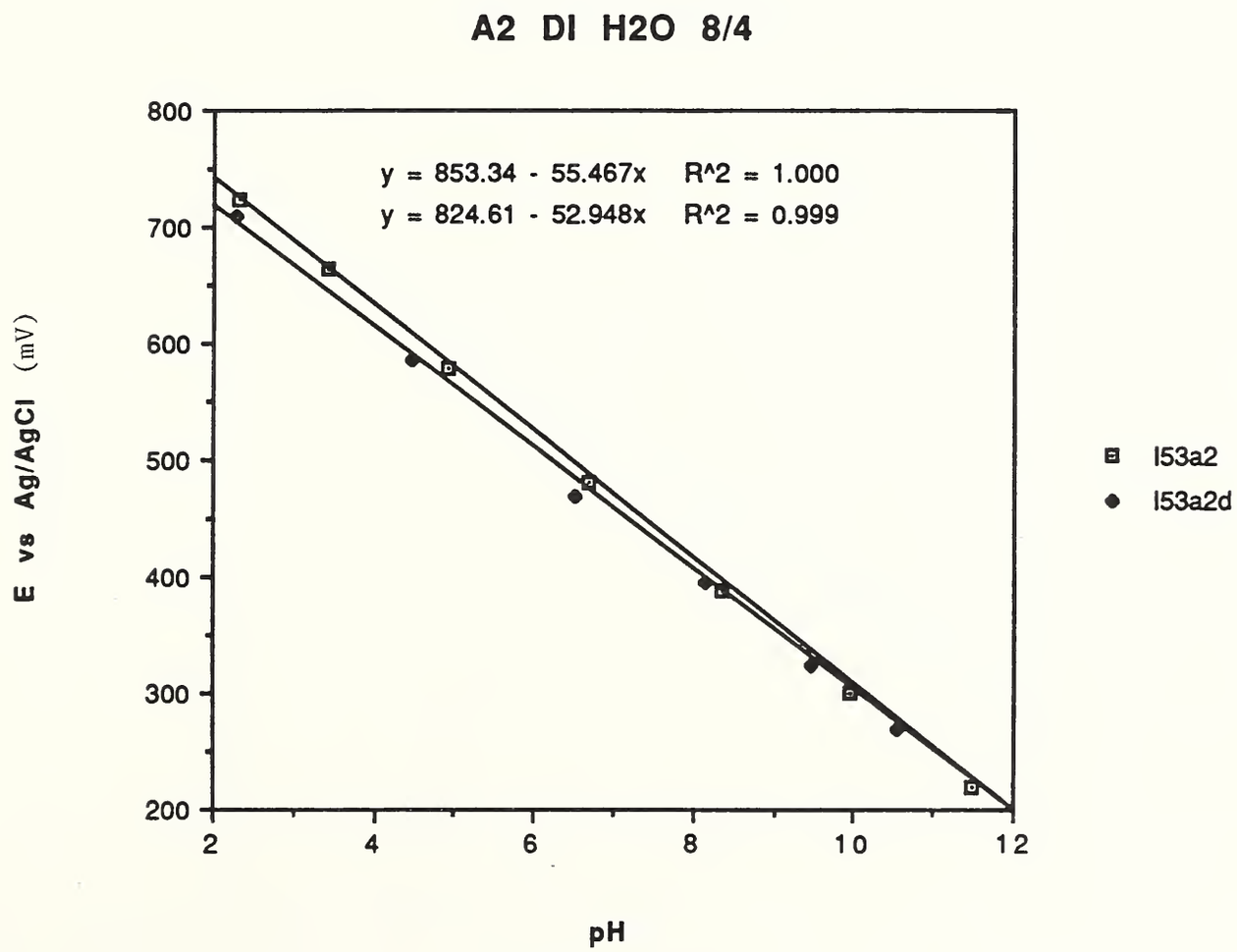

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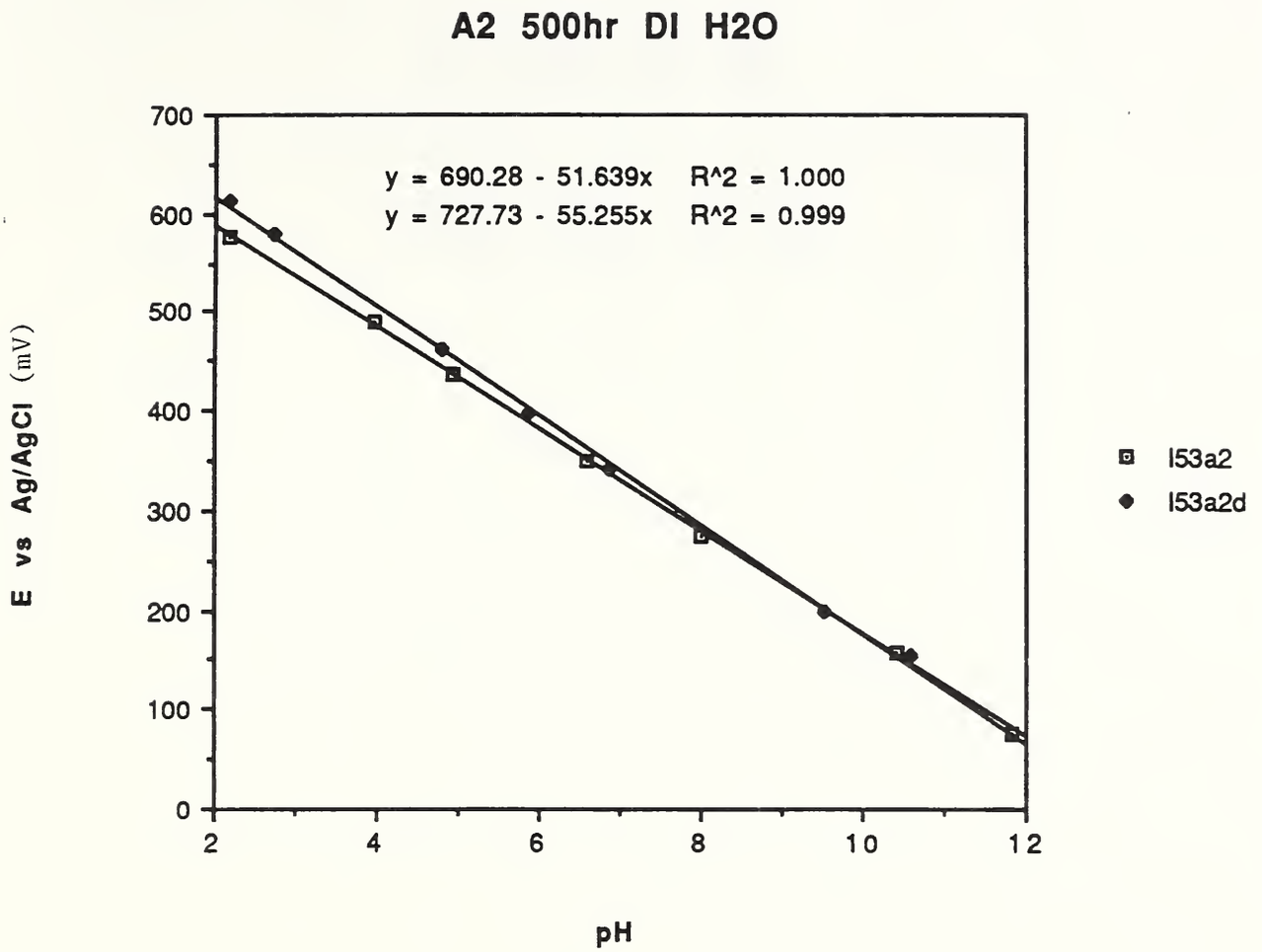

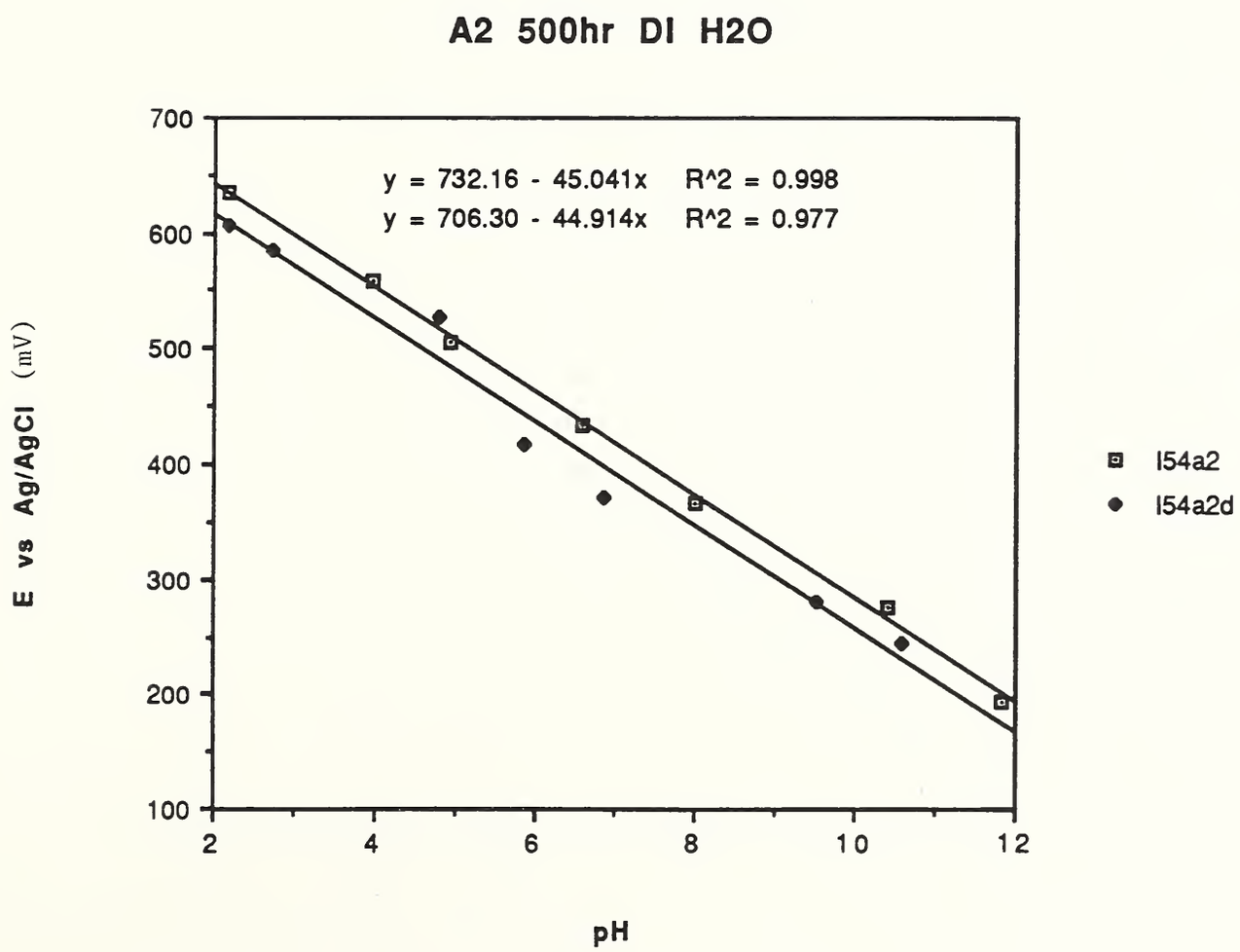

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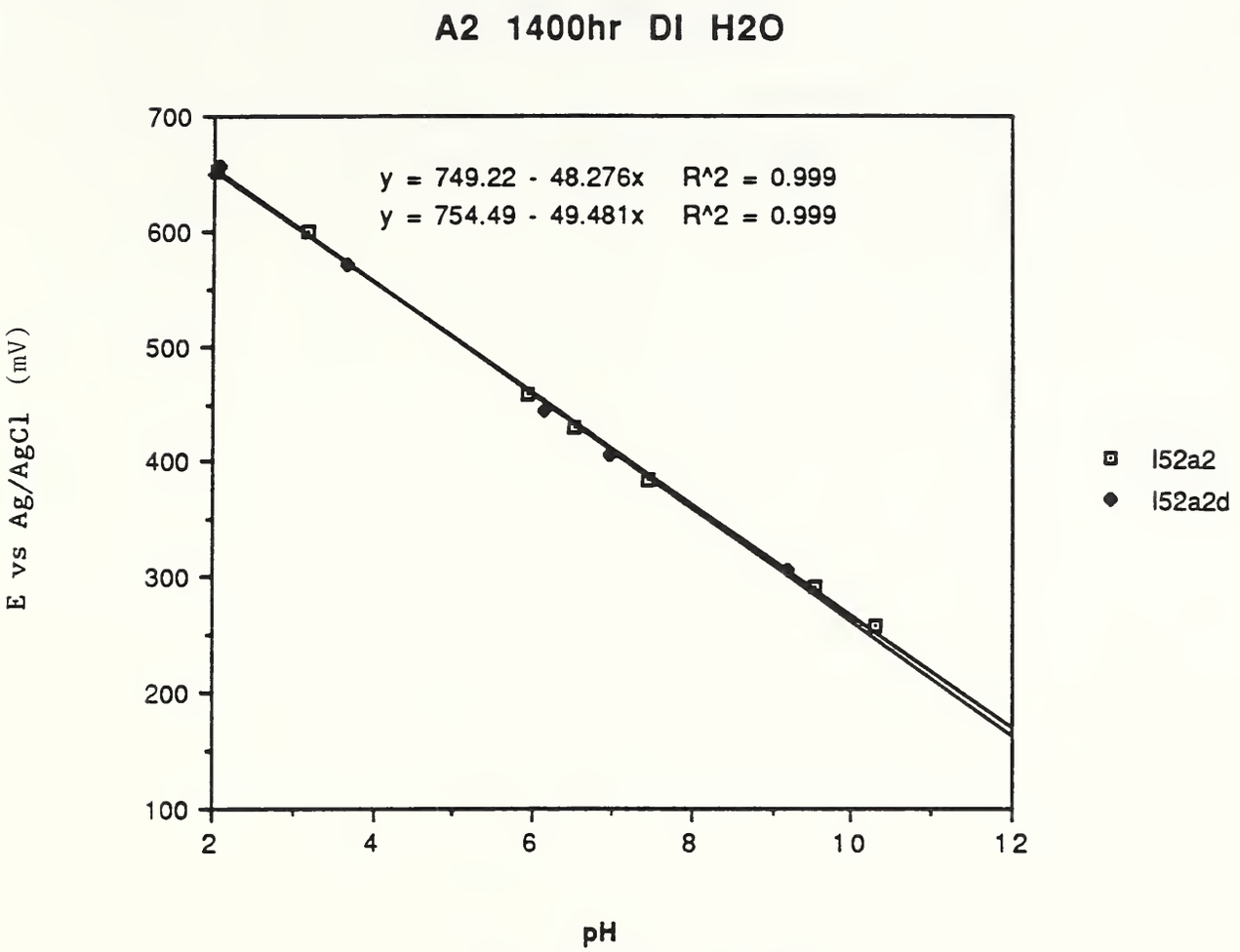

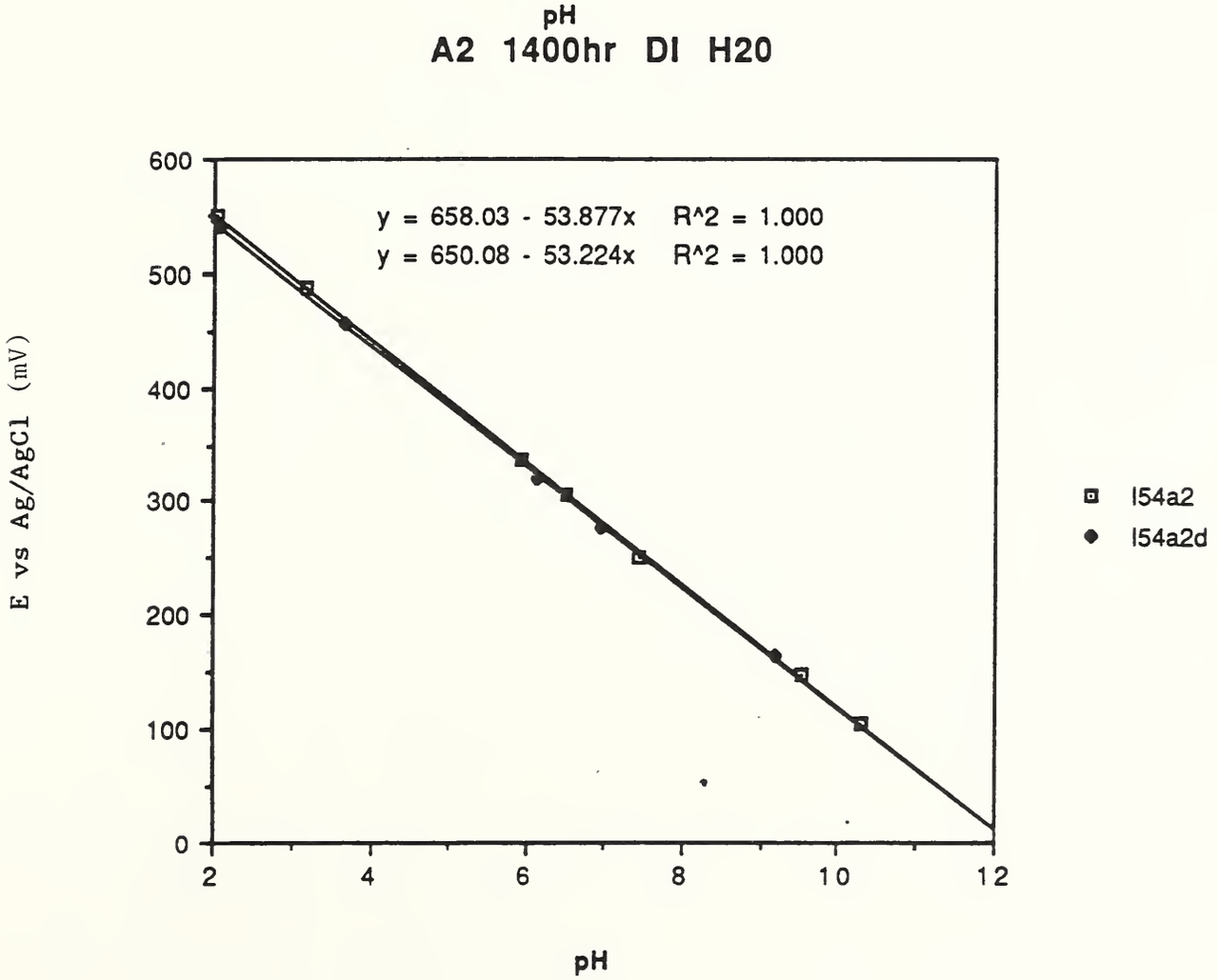

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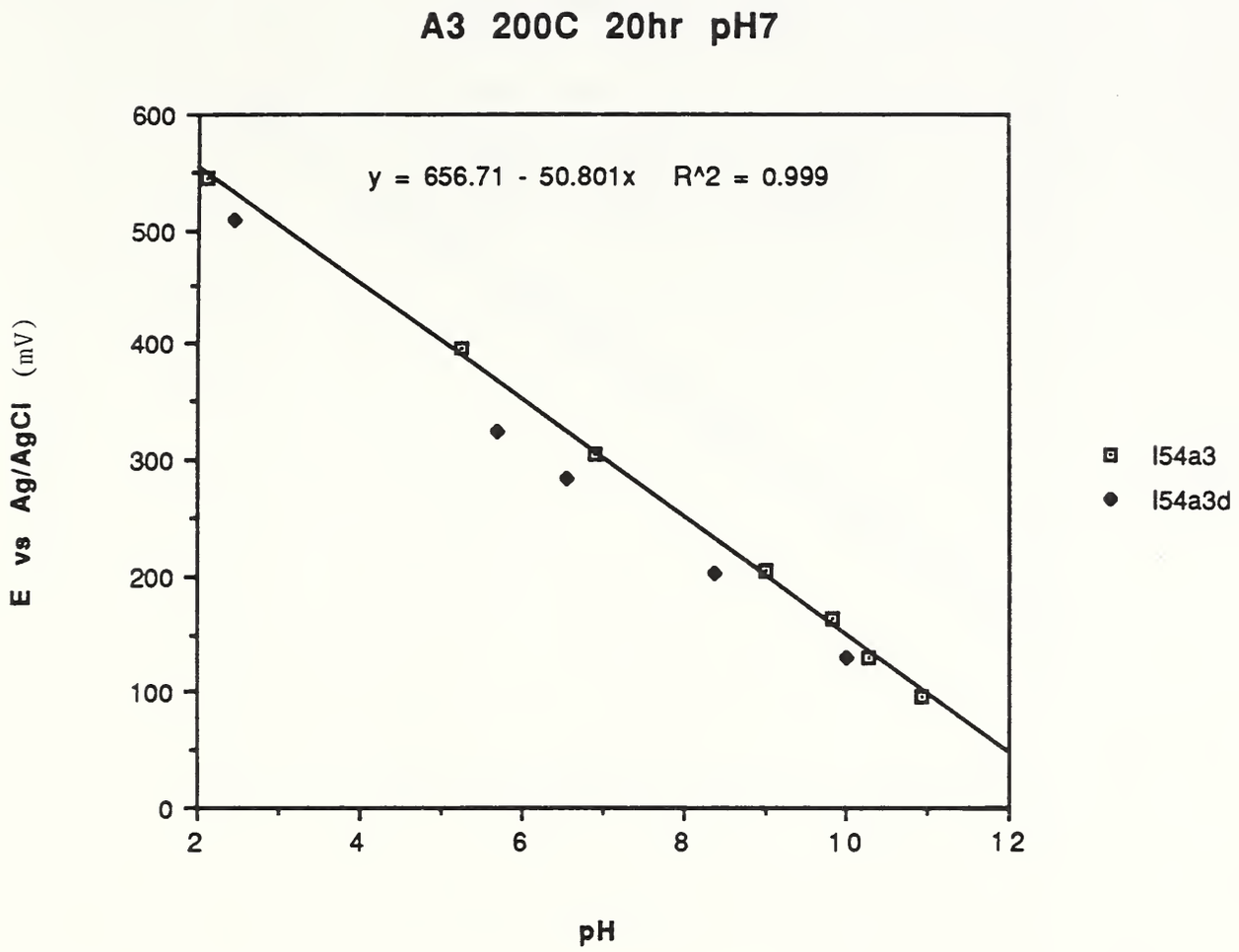

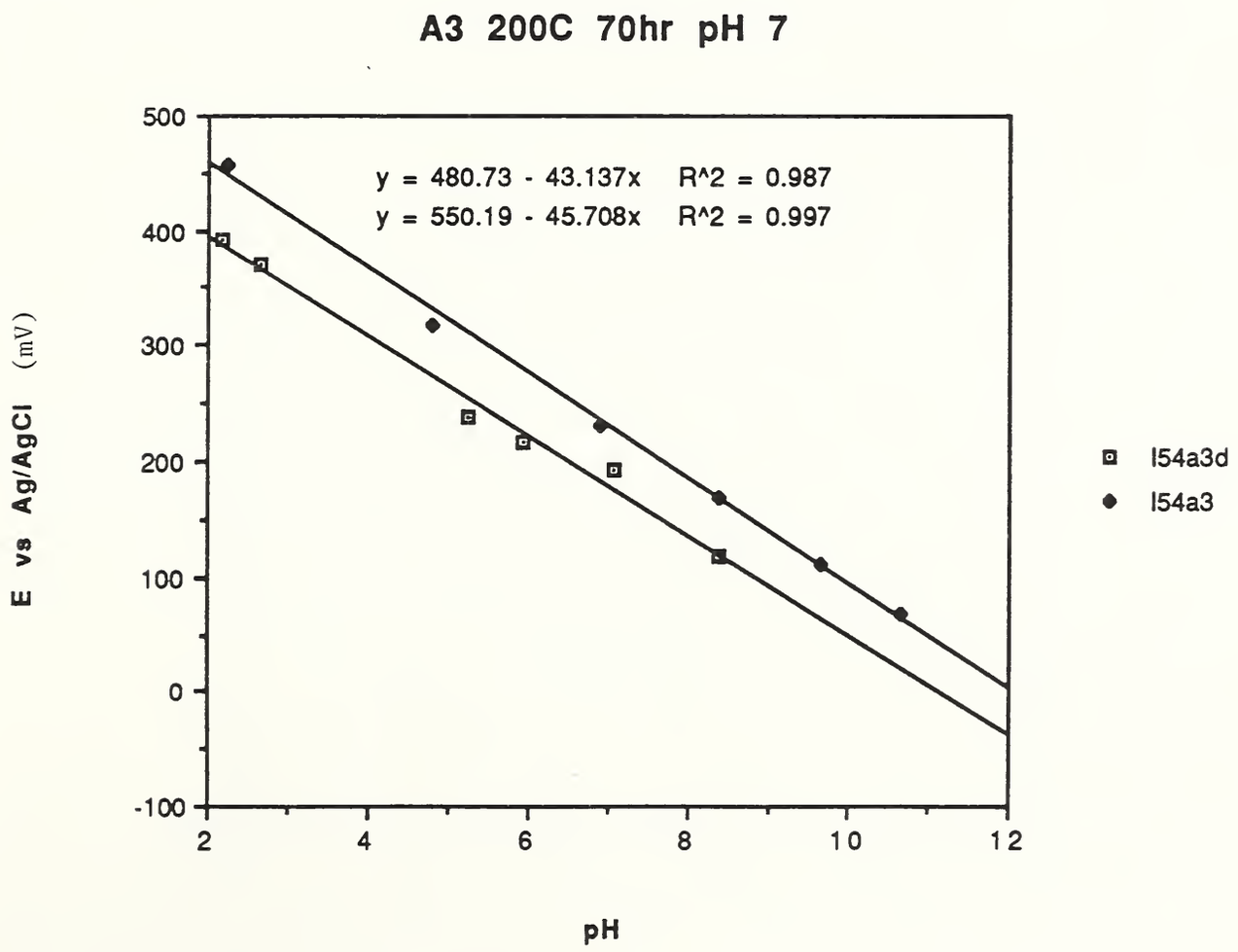

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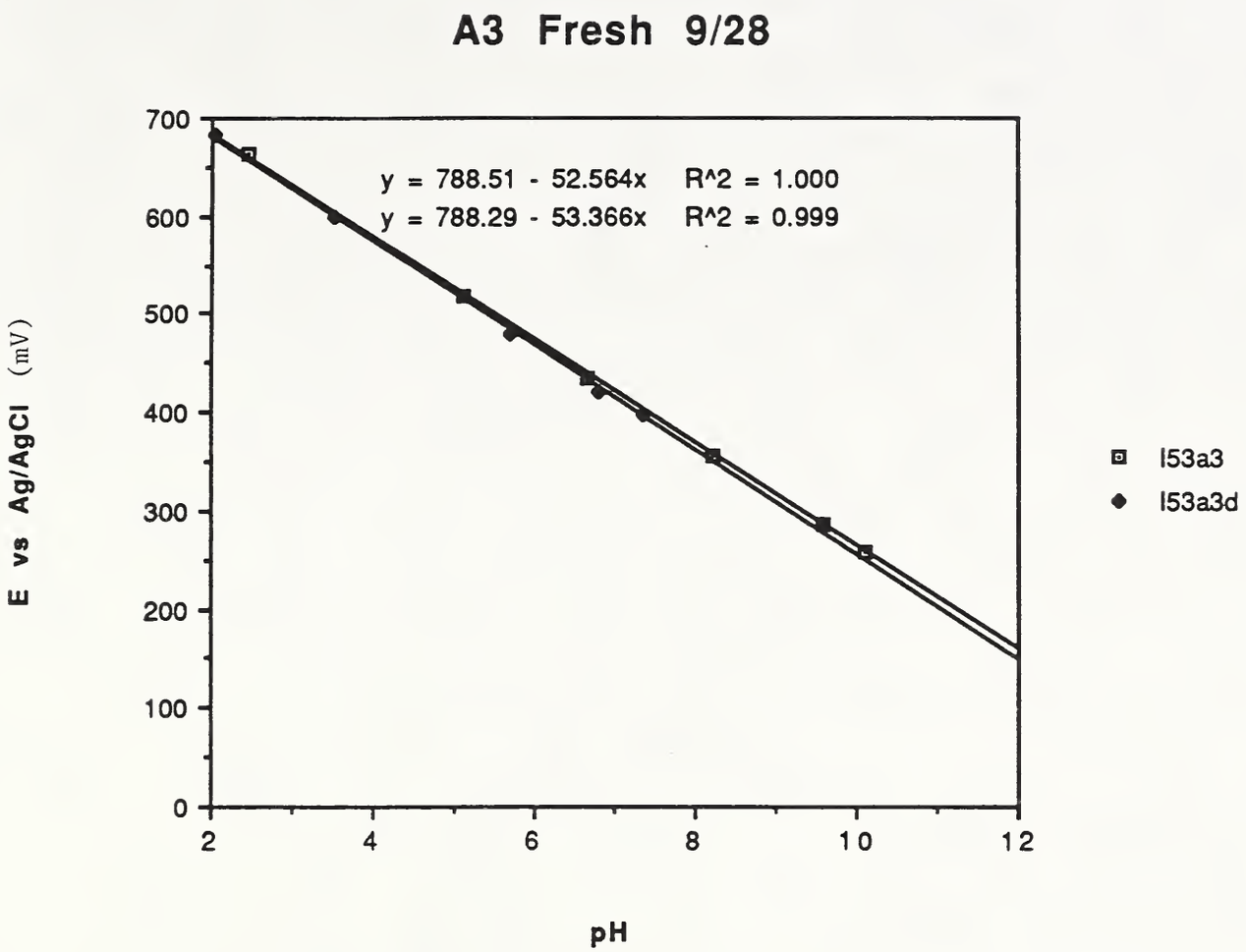

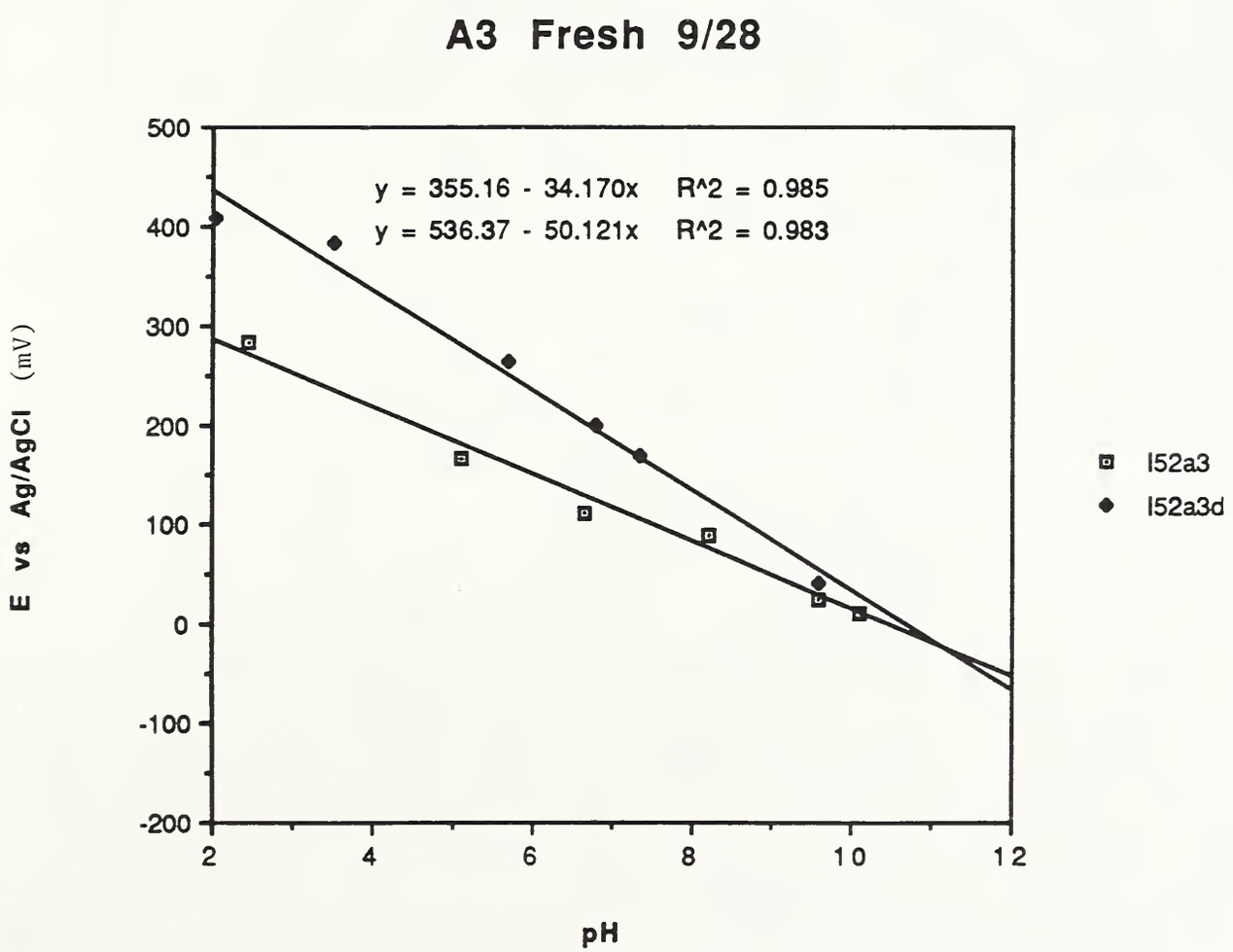

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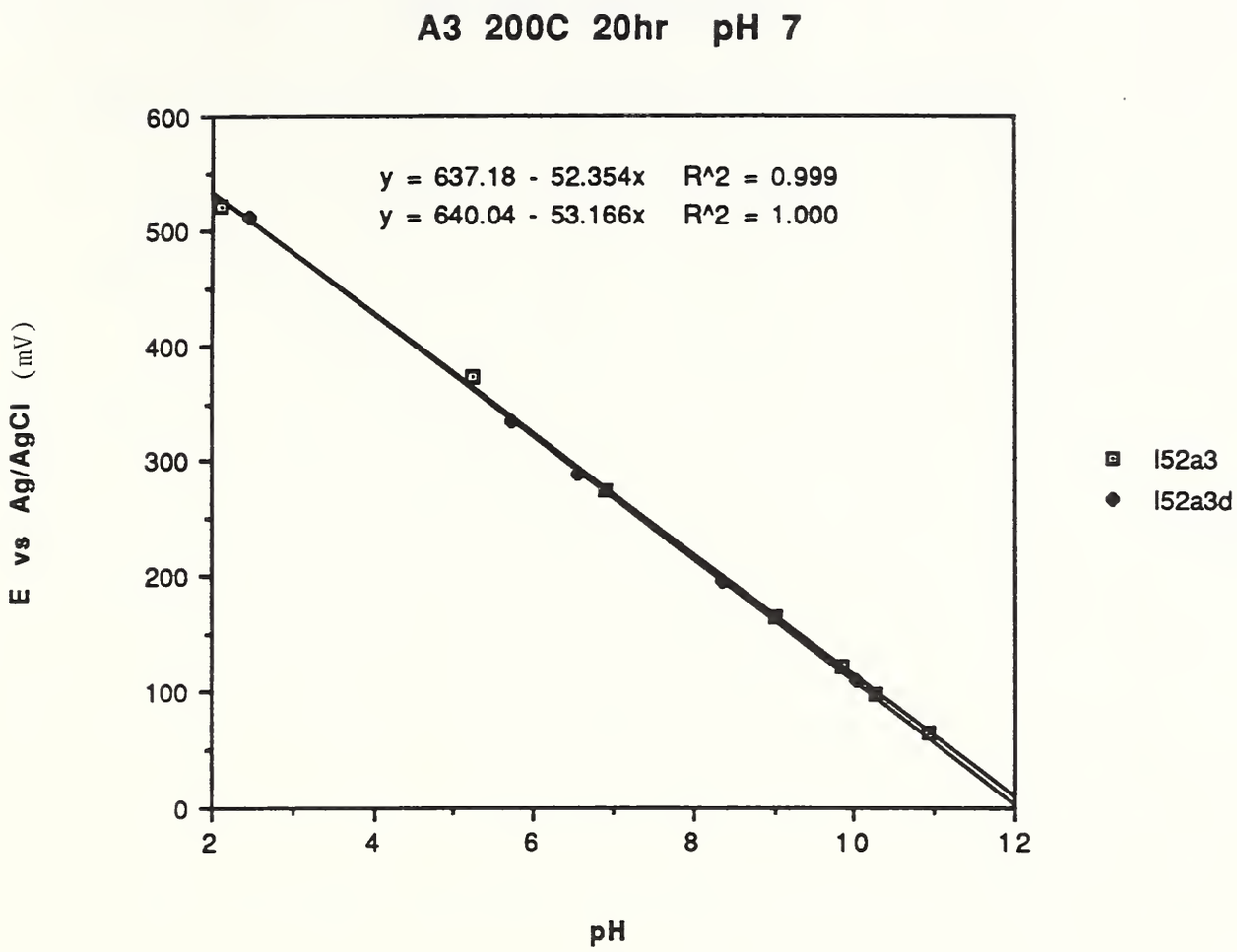

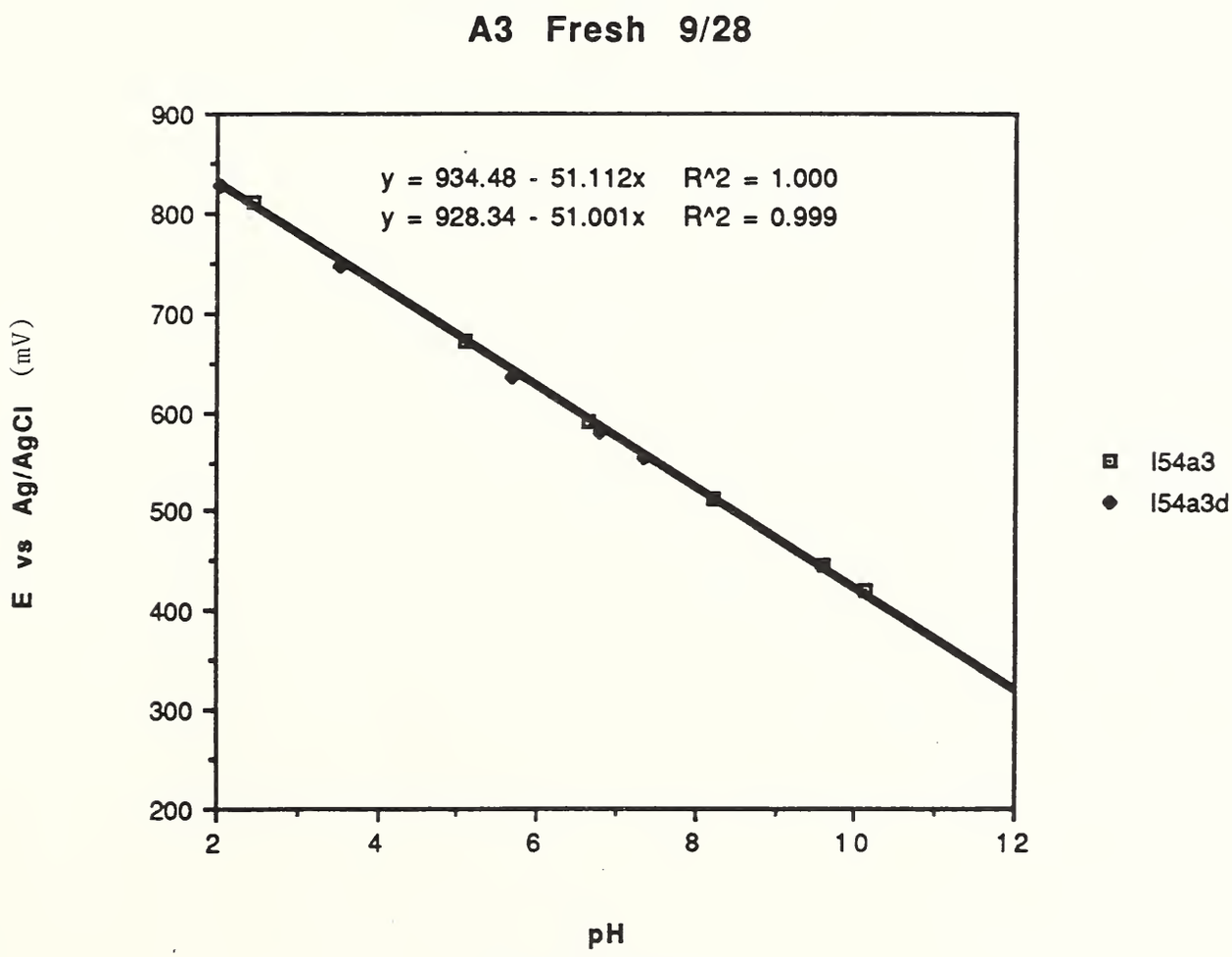

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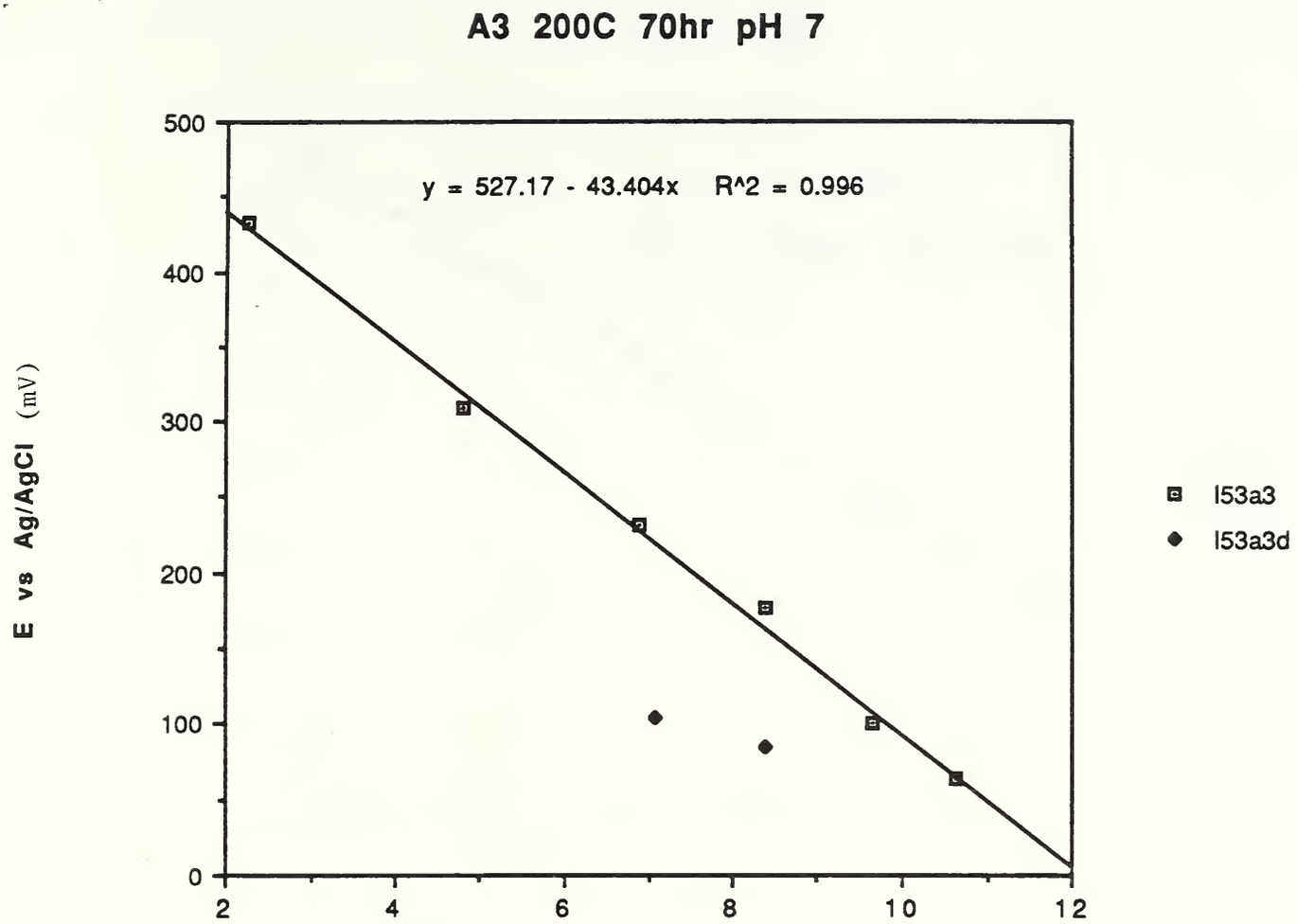

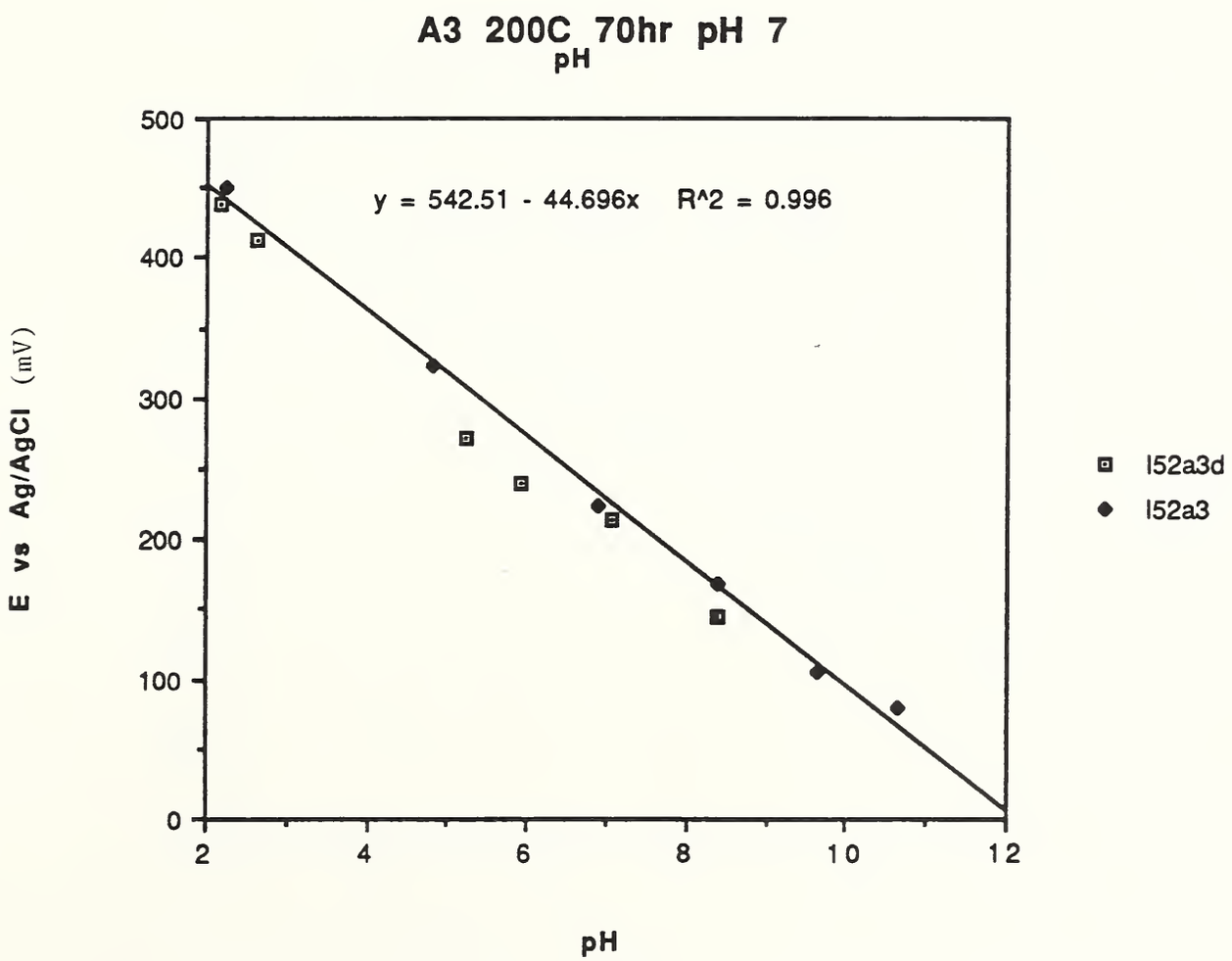

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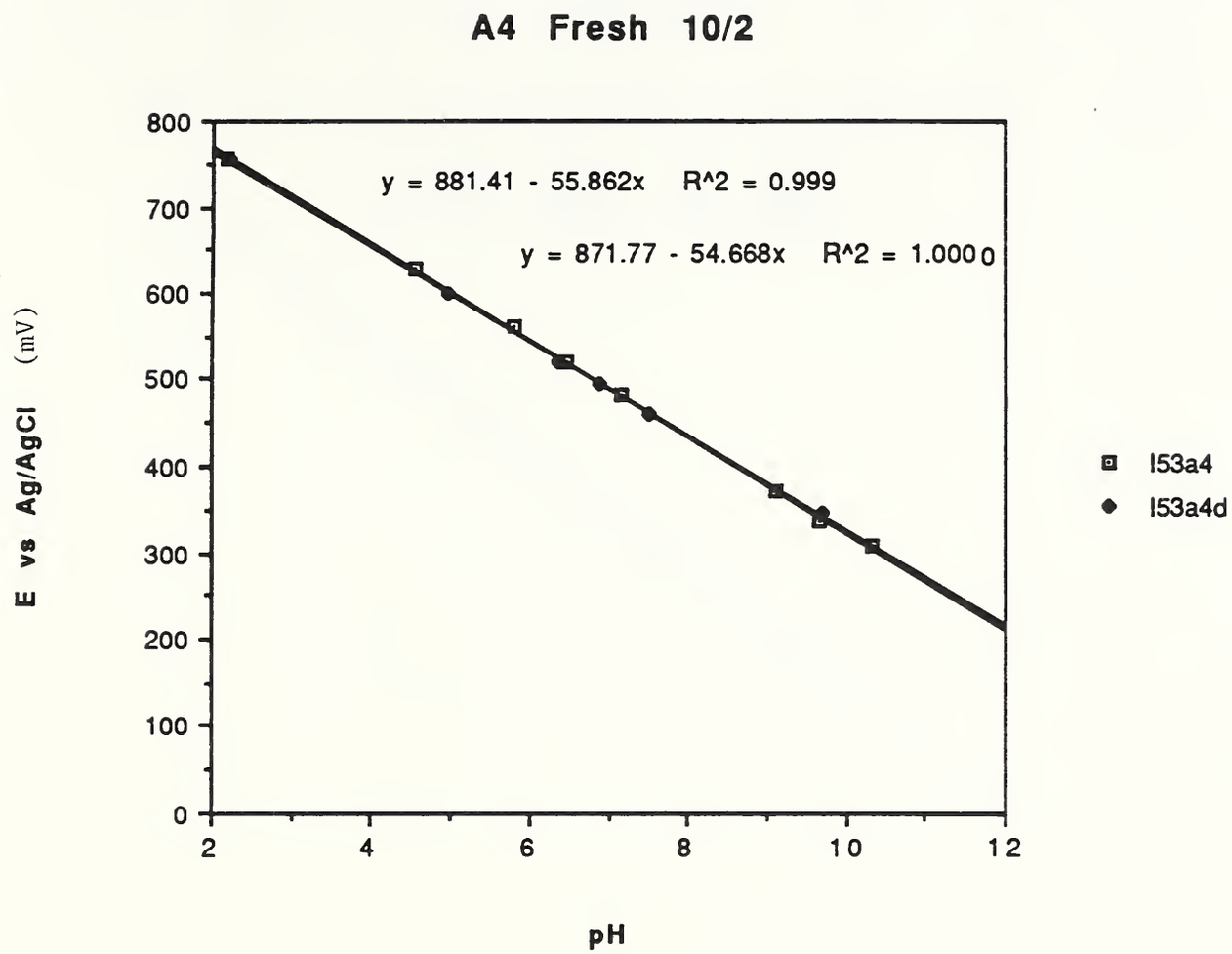
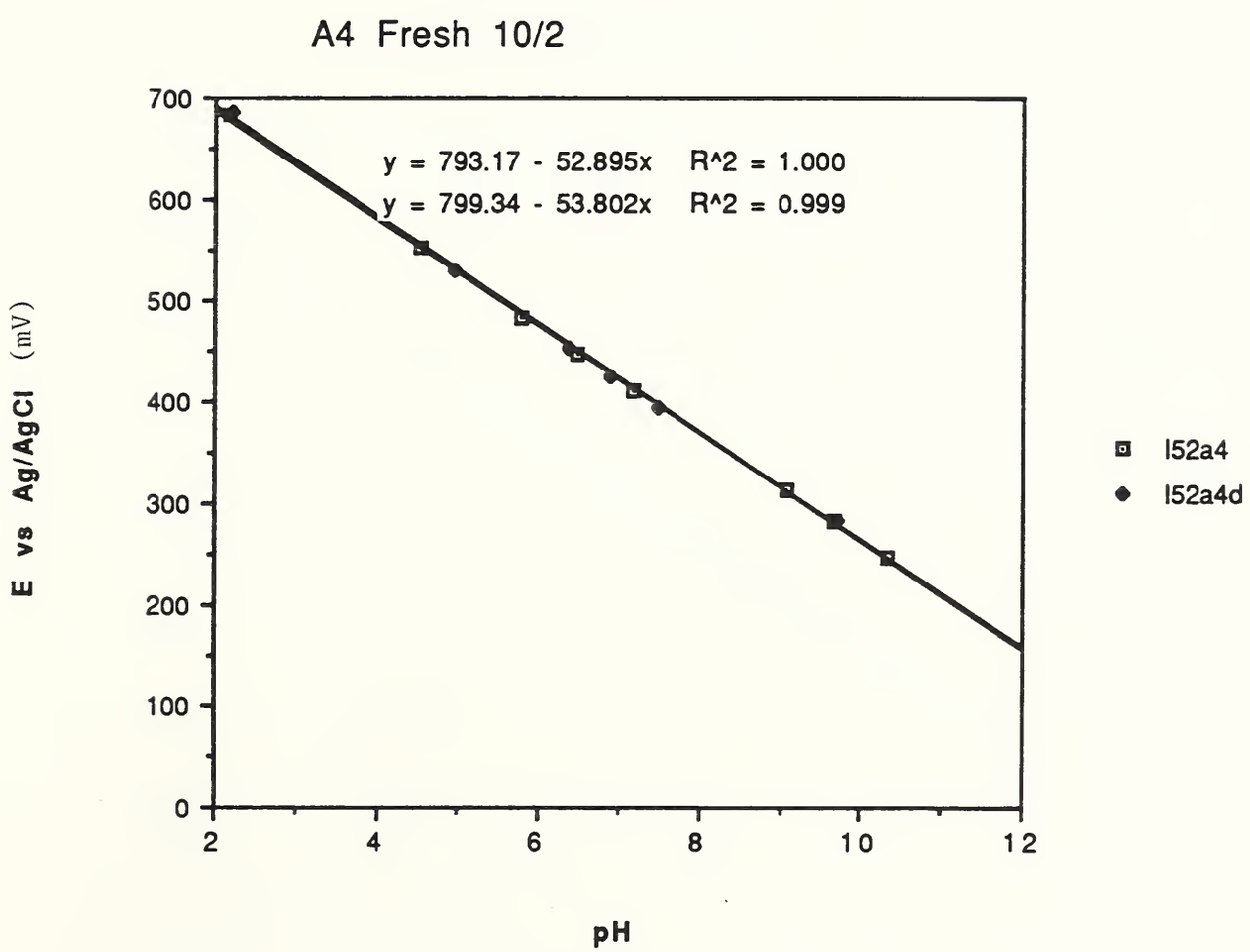
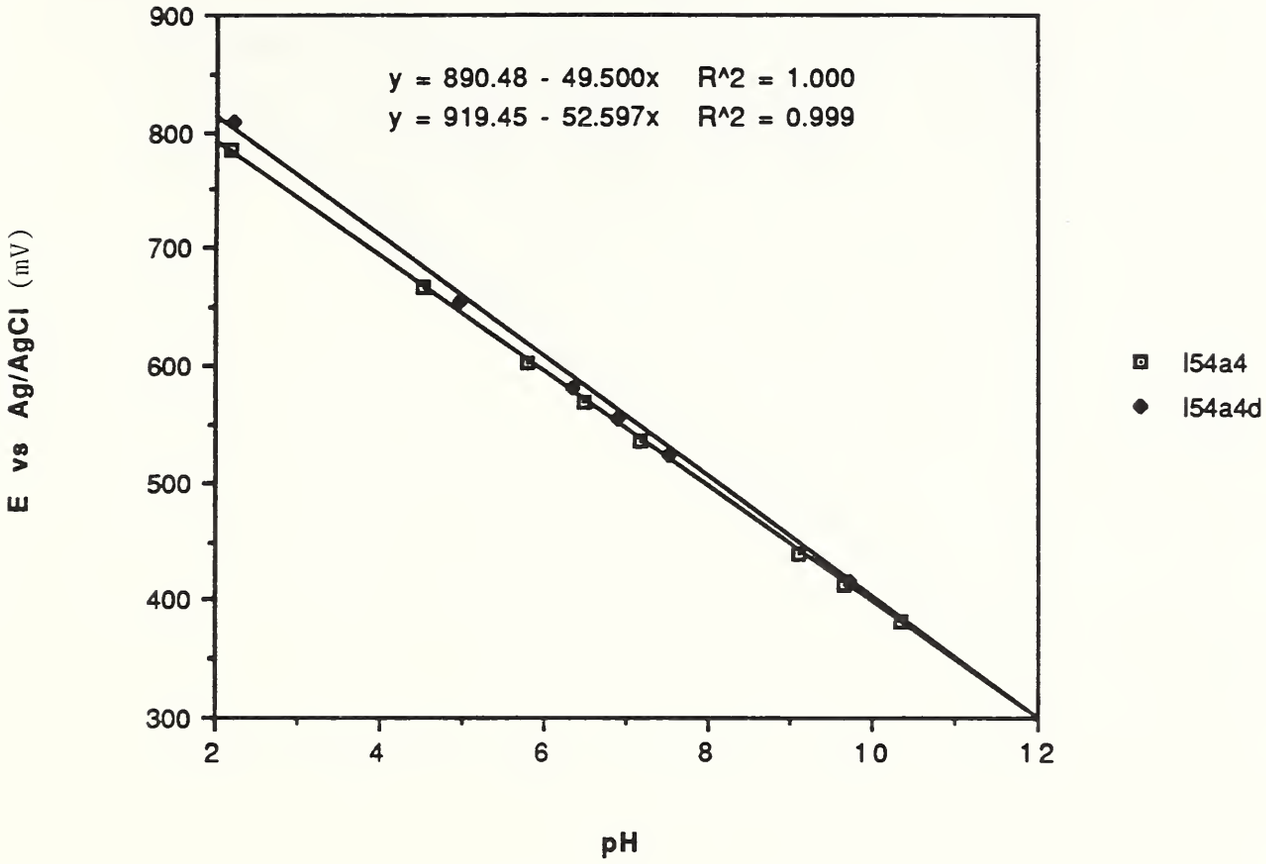


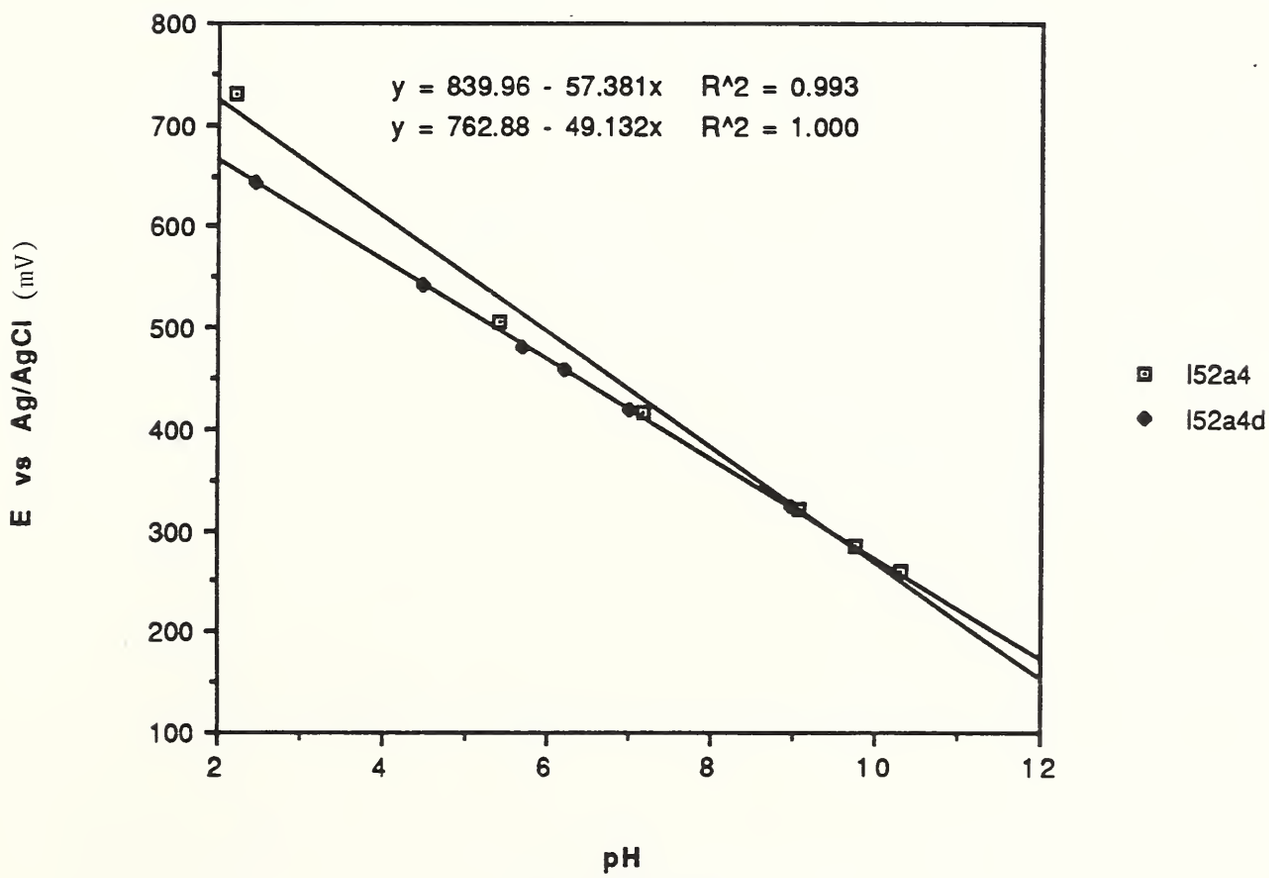


Figures 32-33

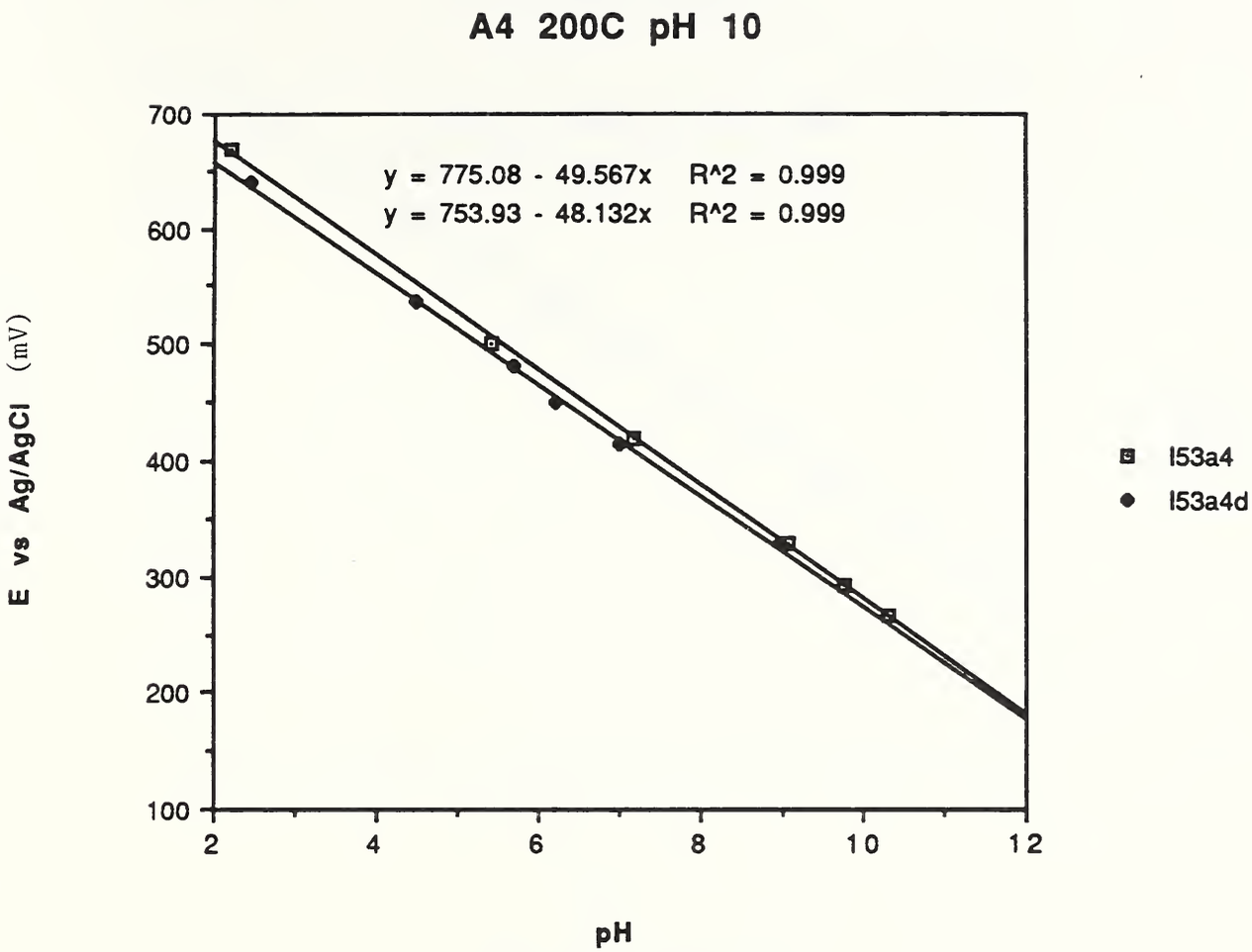
A4 Fresh 10/2

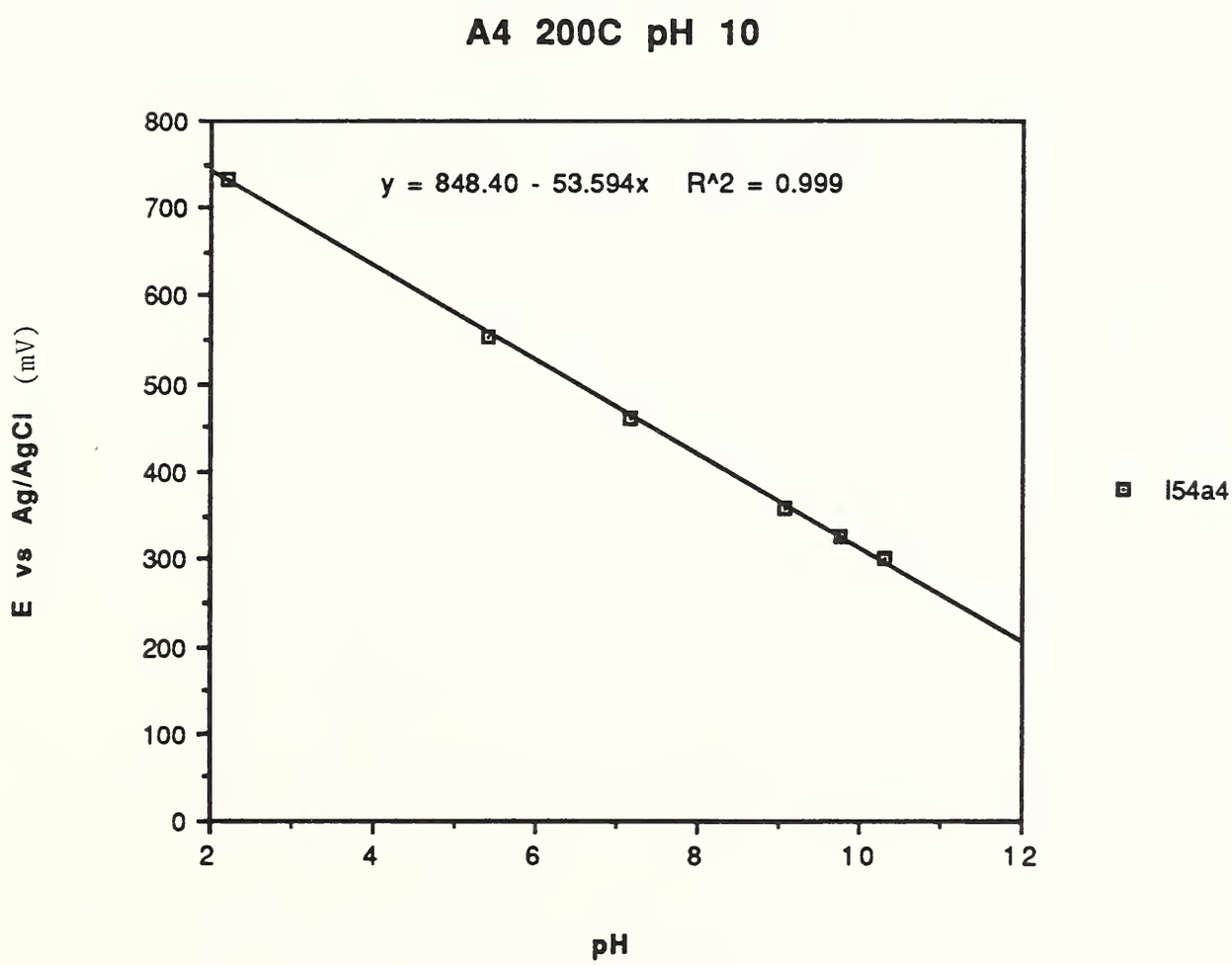


A4 200C pH 10

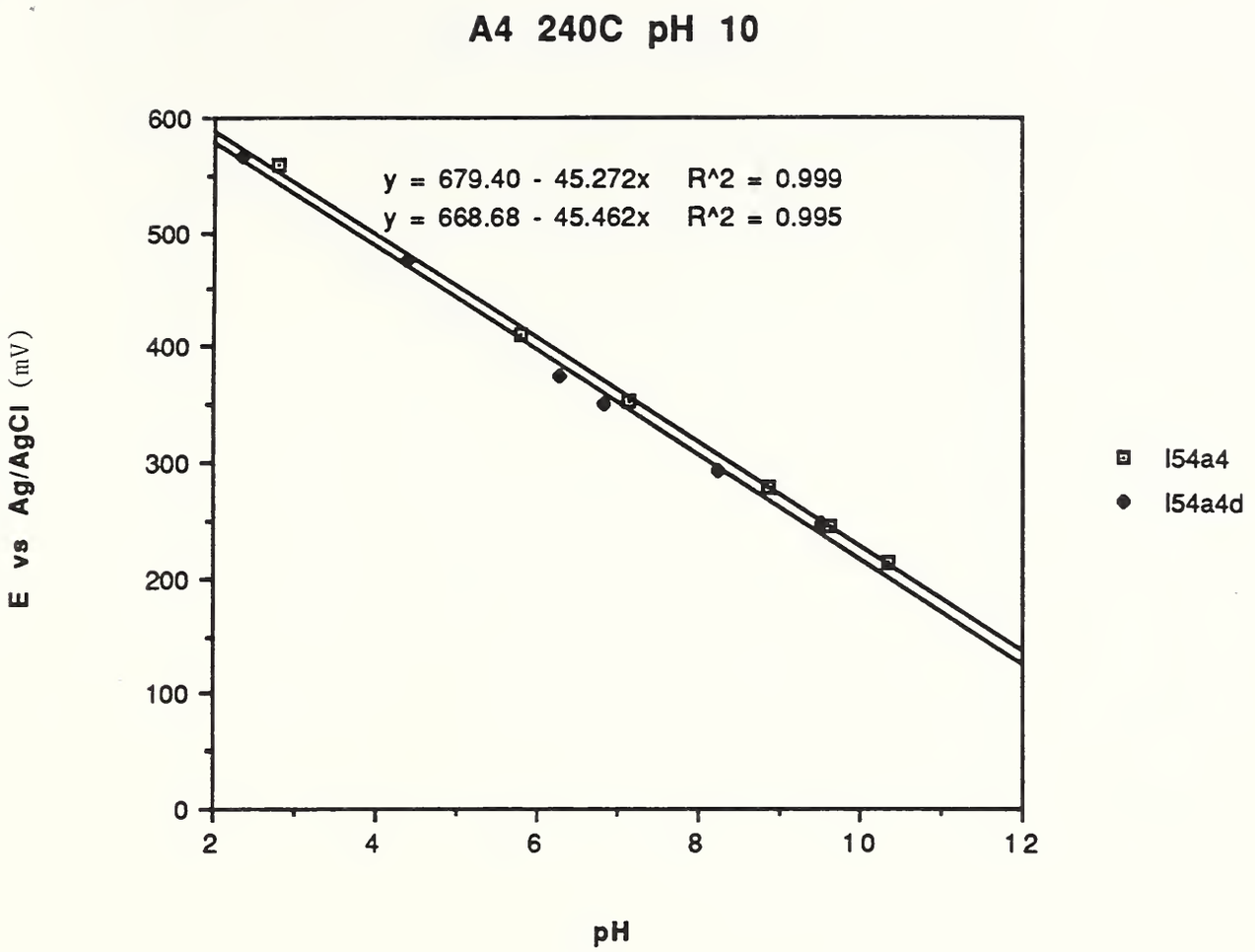


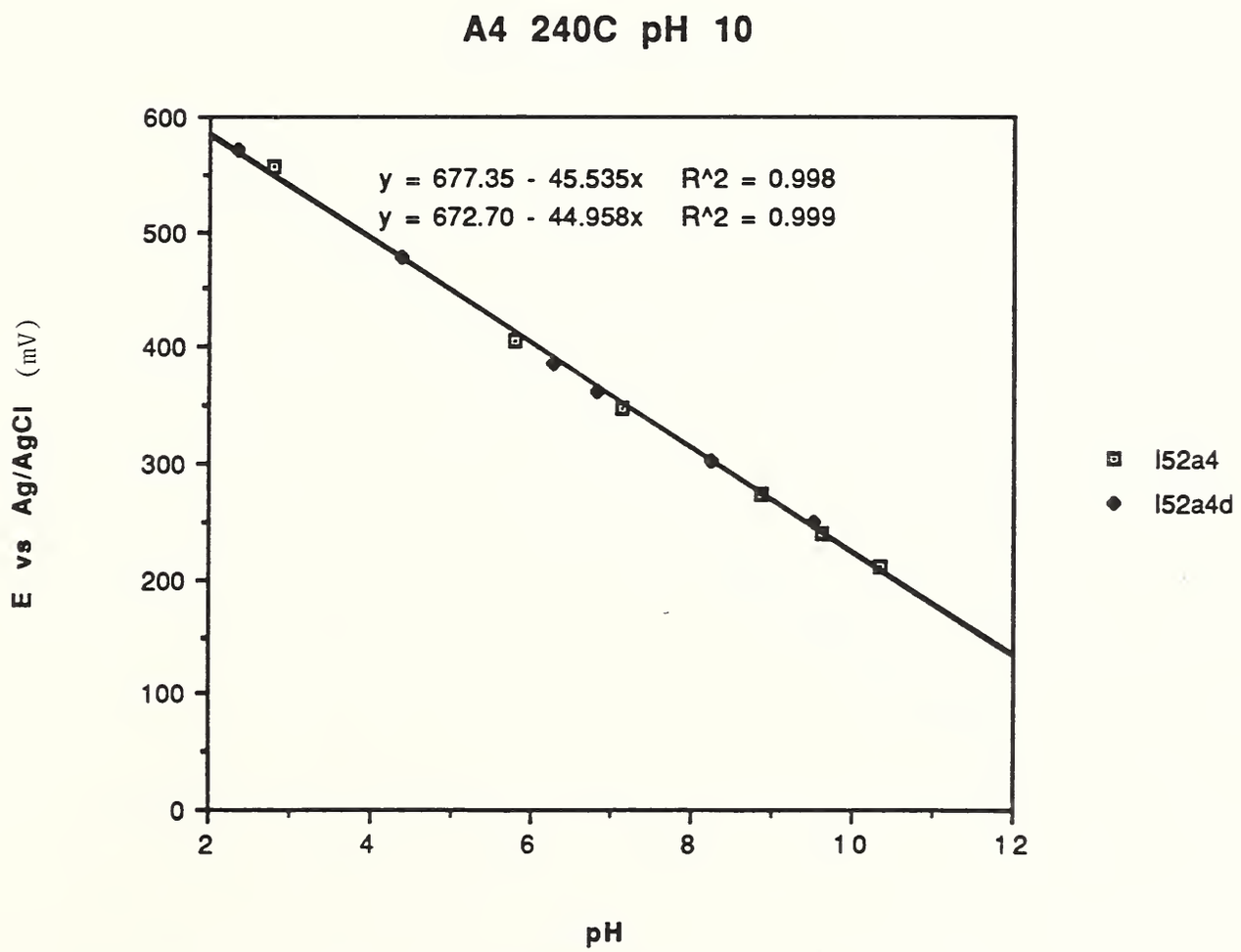
Figures 34-35



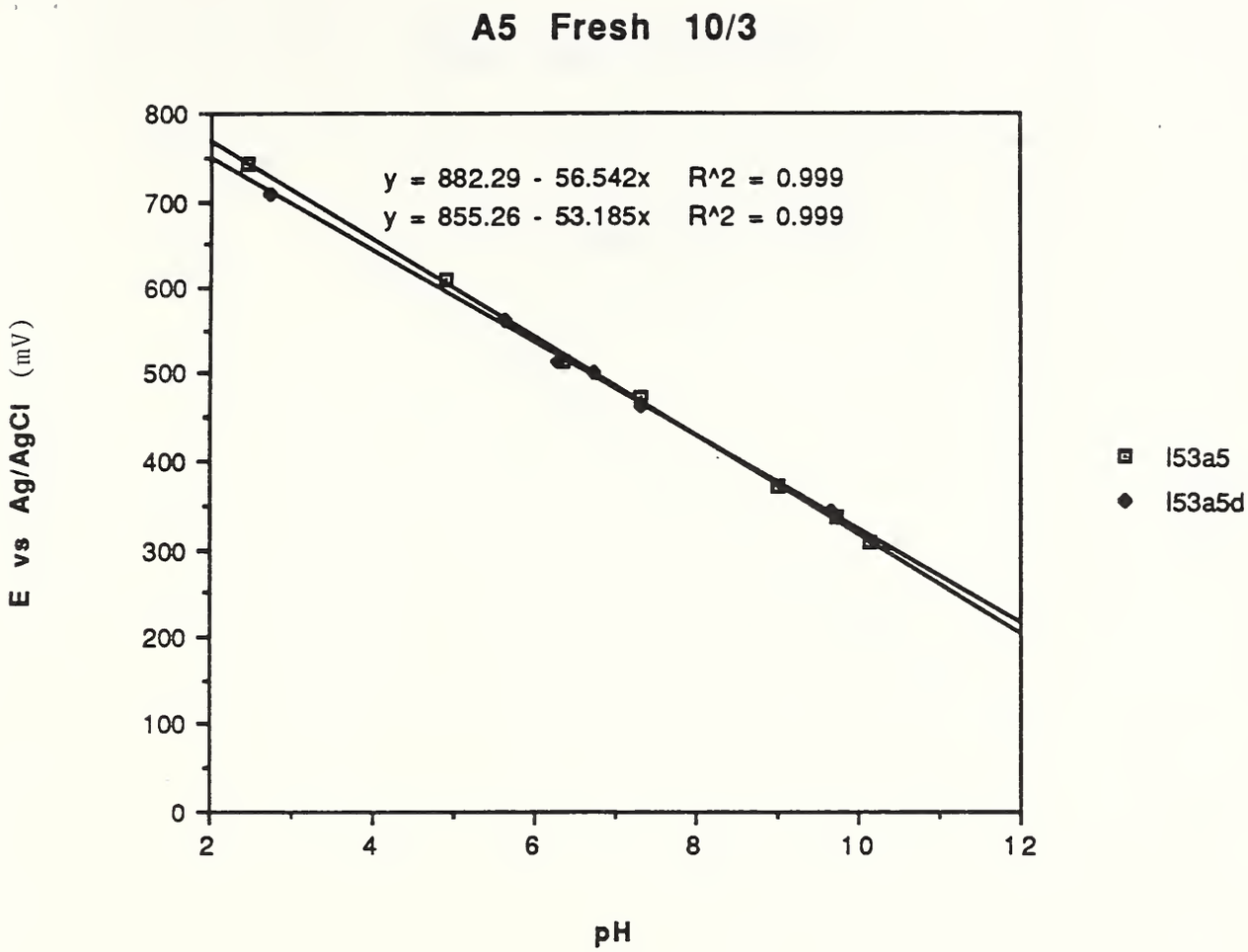


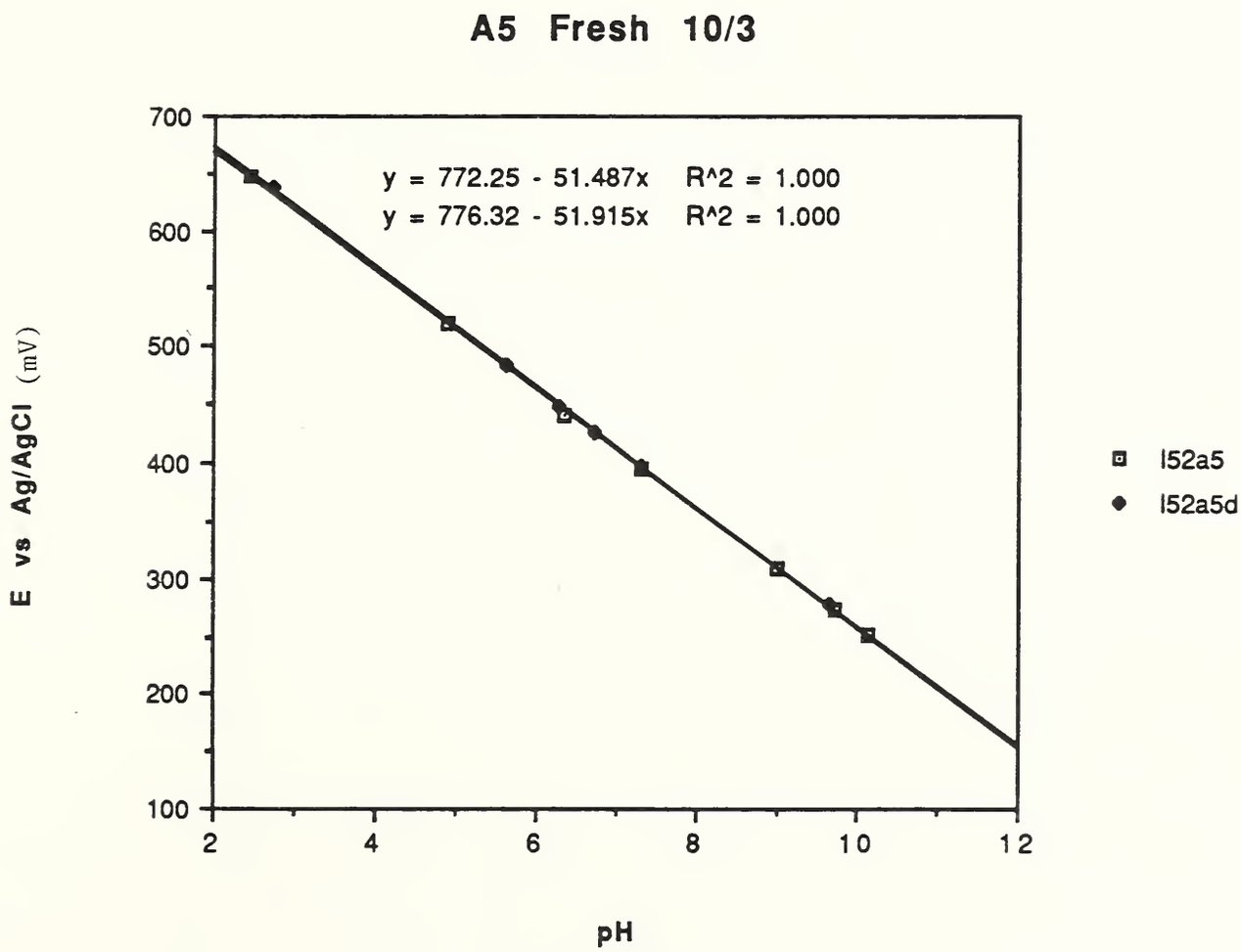
Figures 36-37



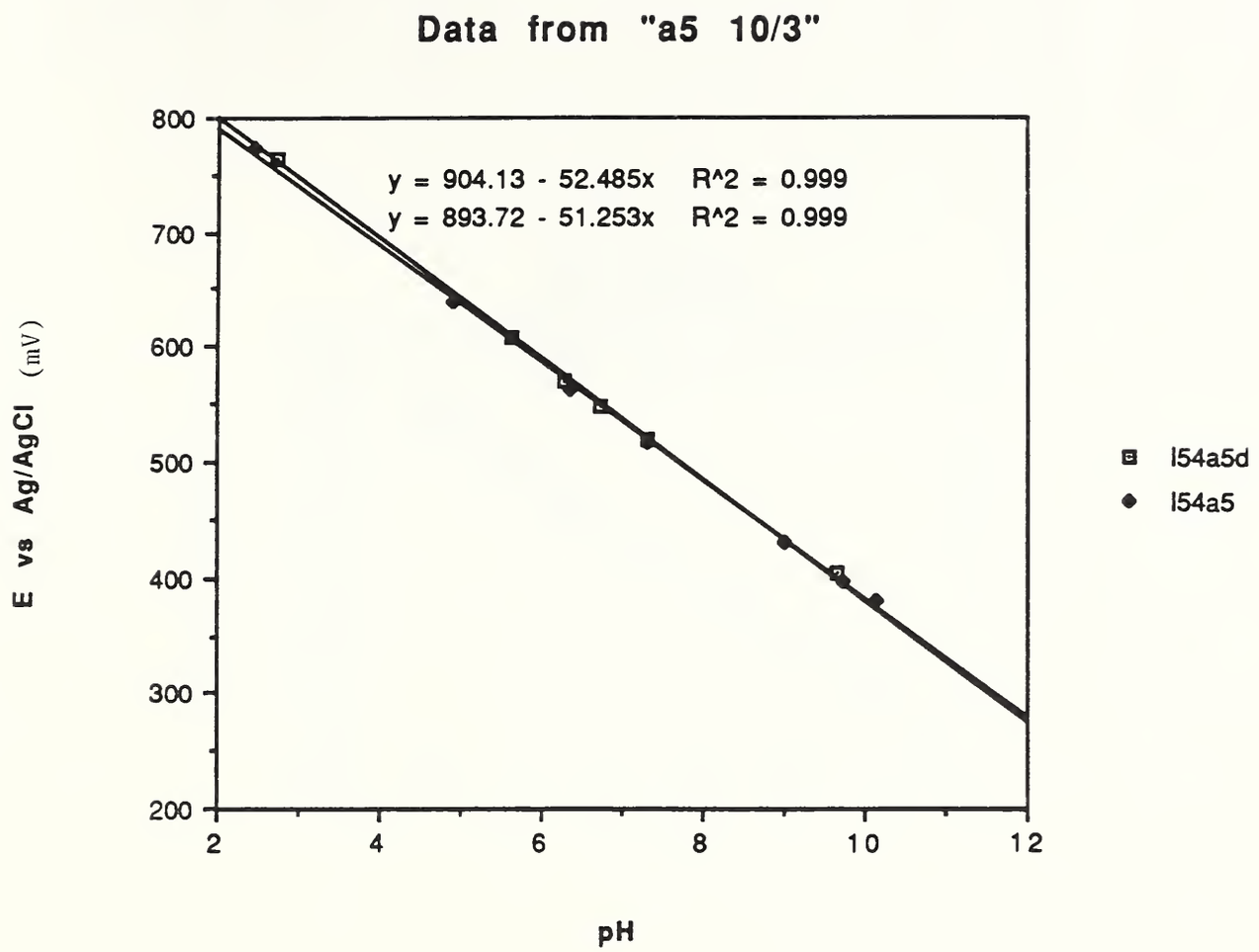


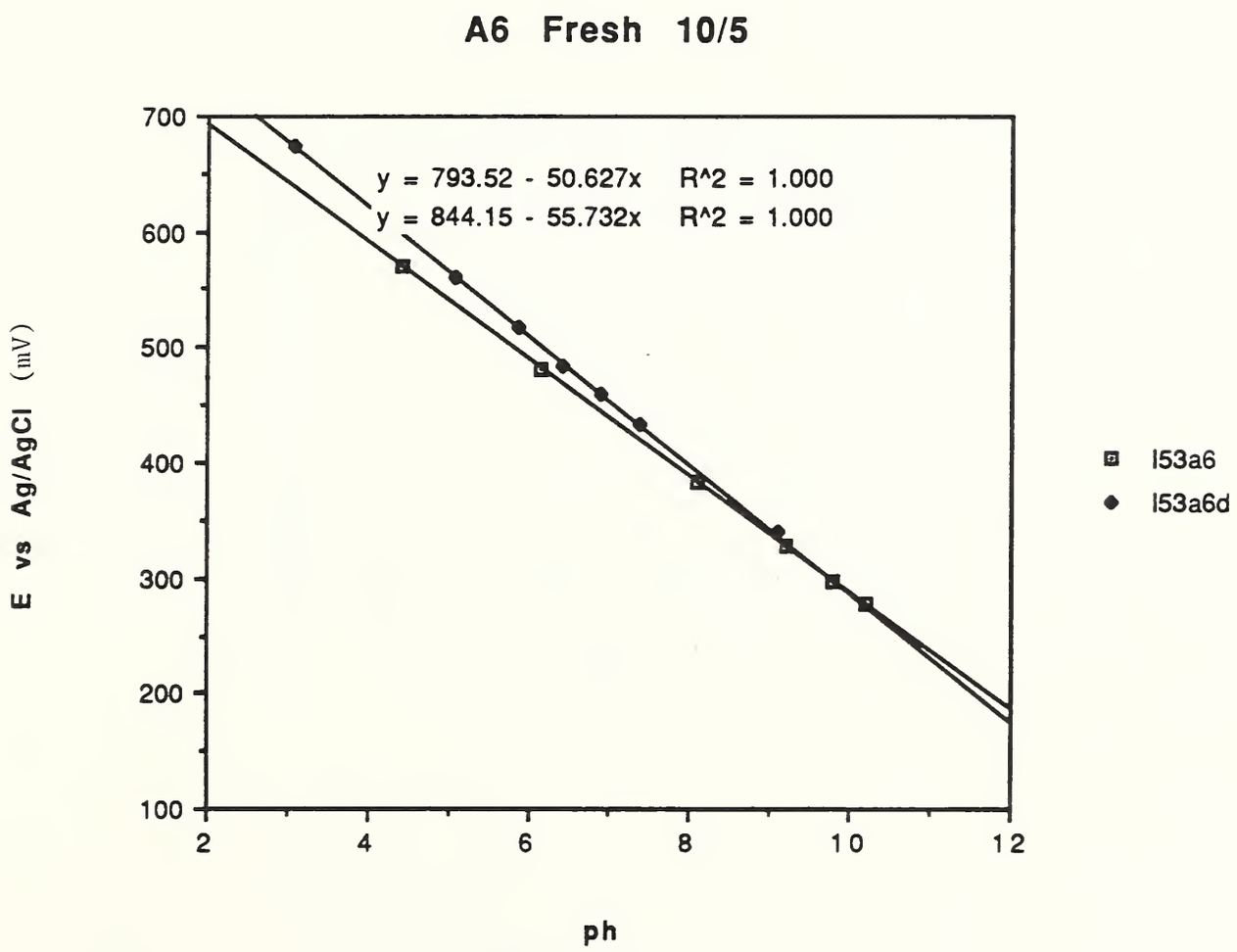
Figures 38-39



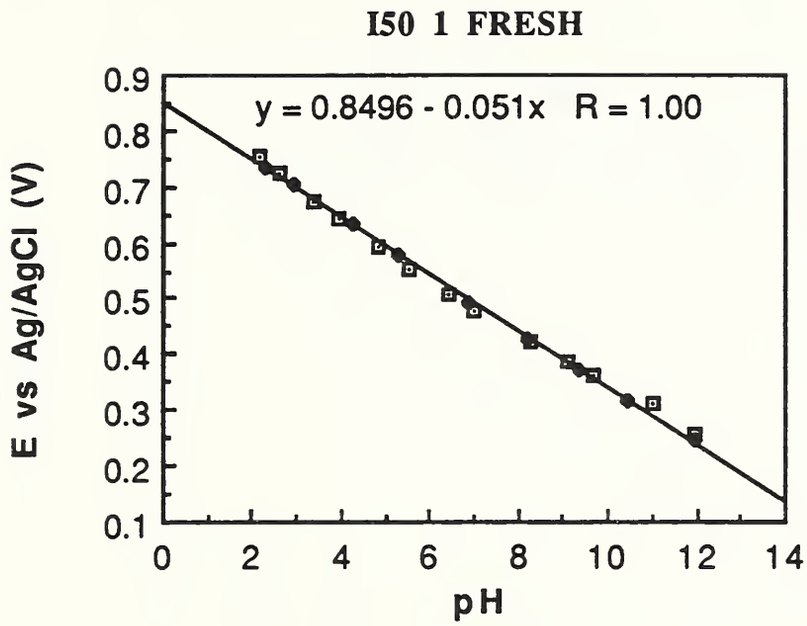


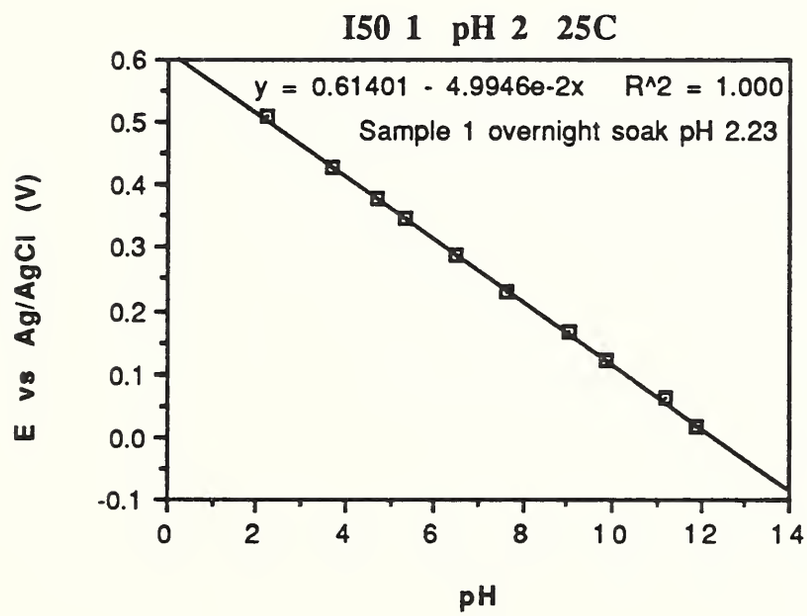
Figures 40-41



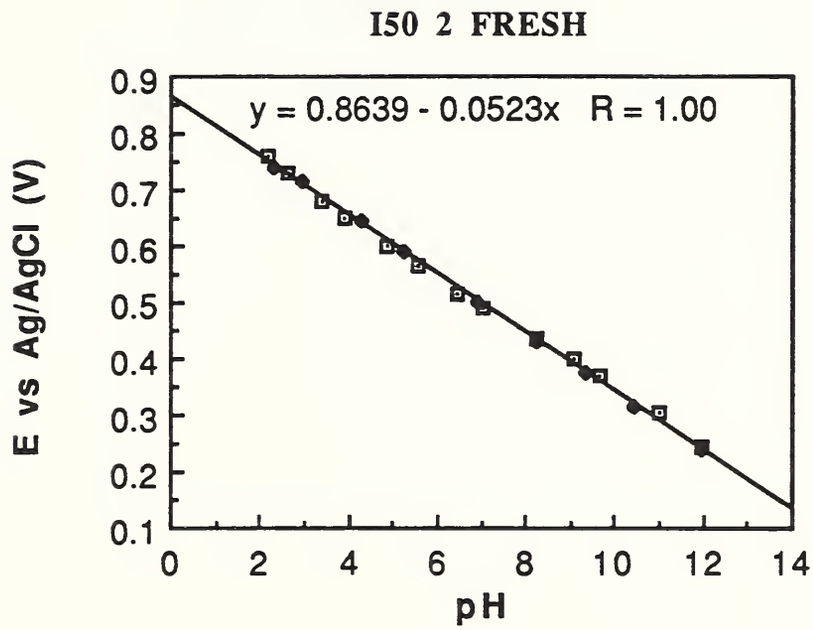


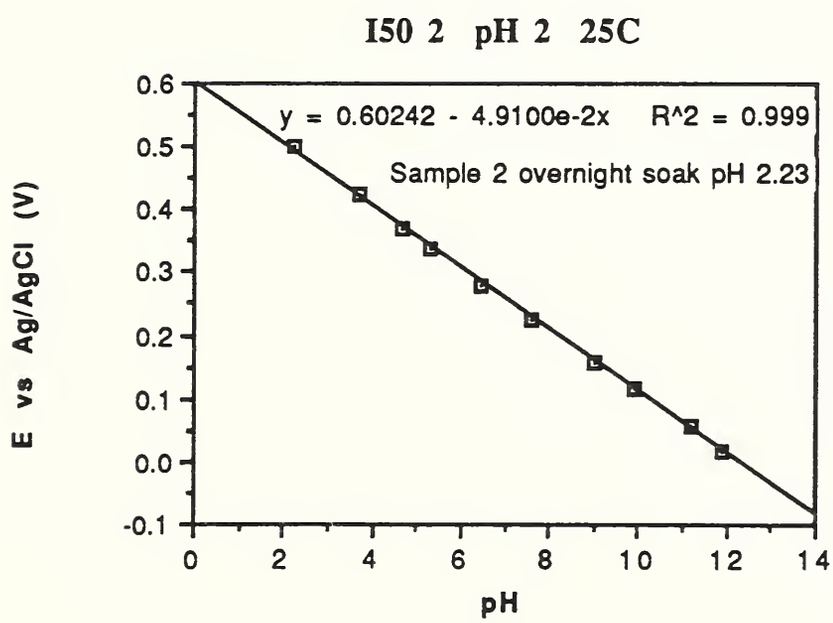
Figures 42-43



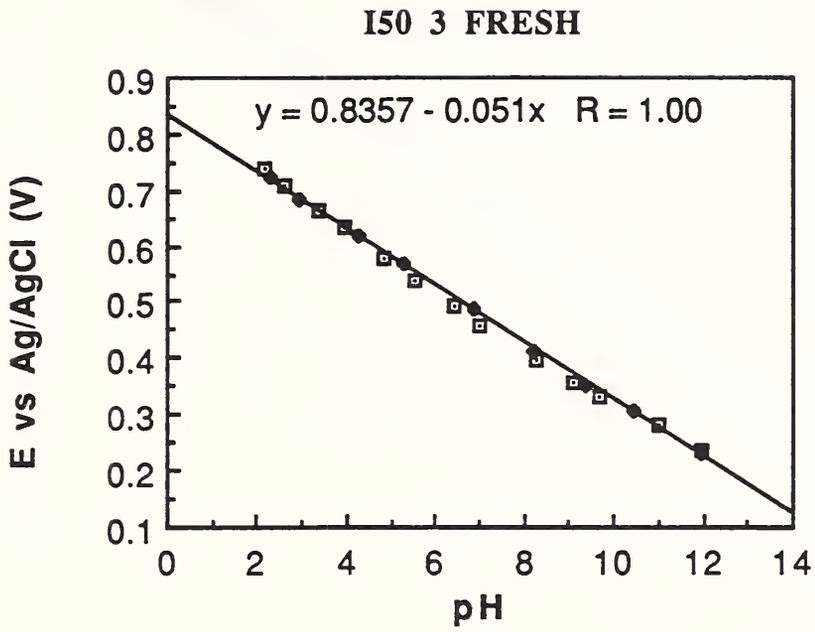


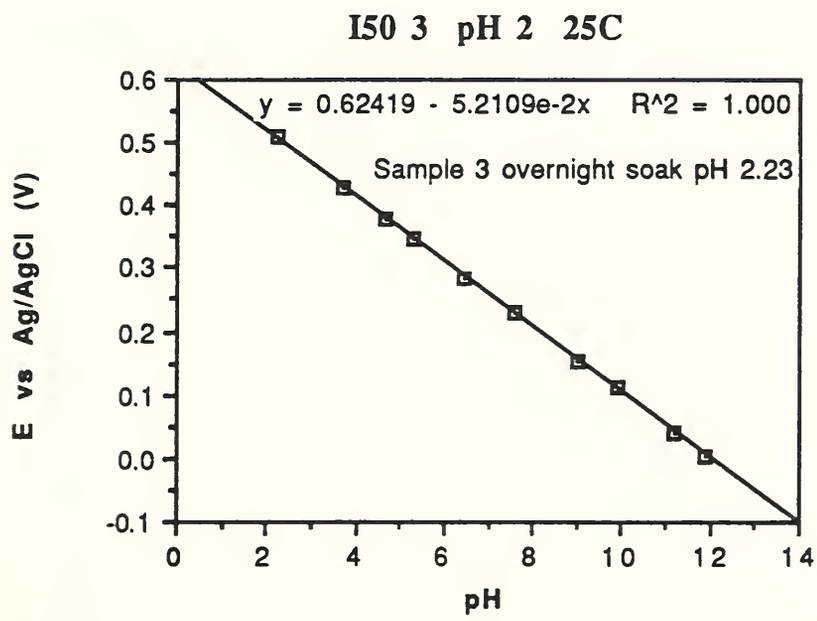
Figures 44-45



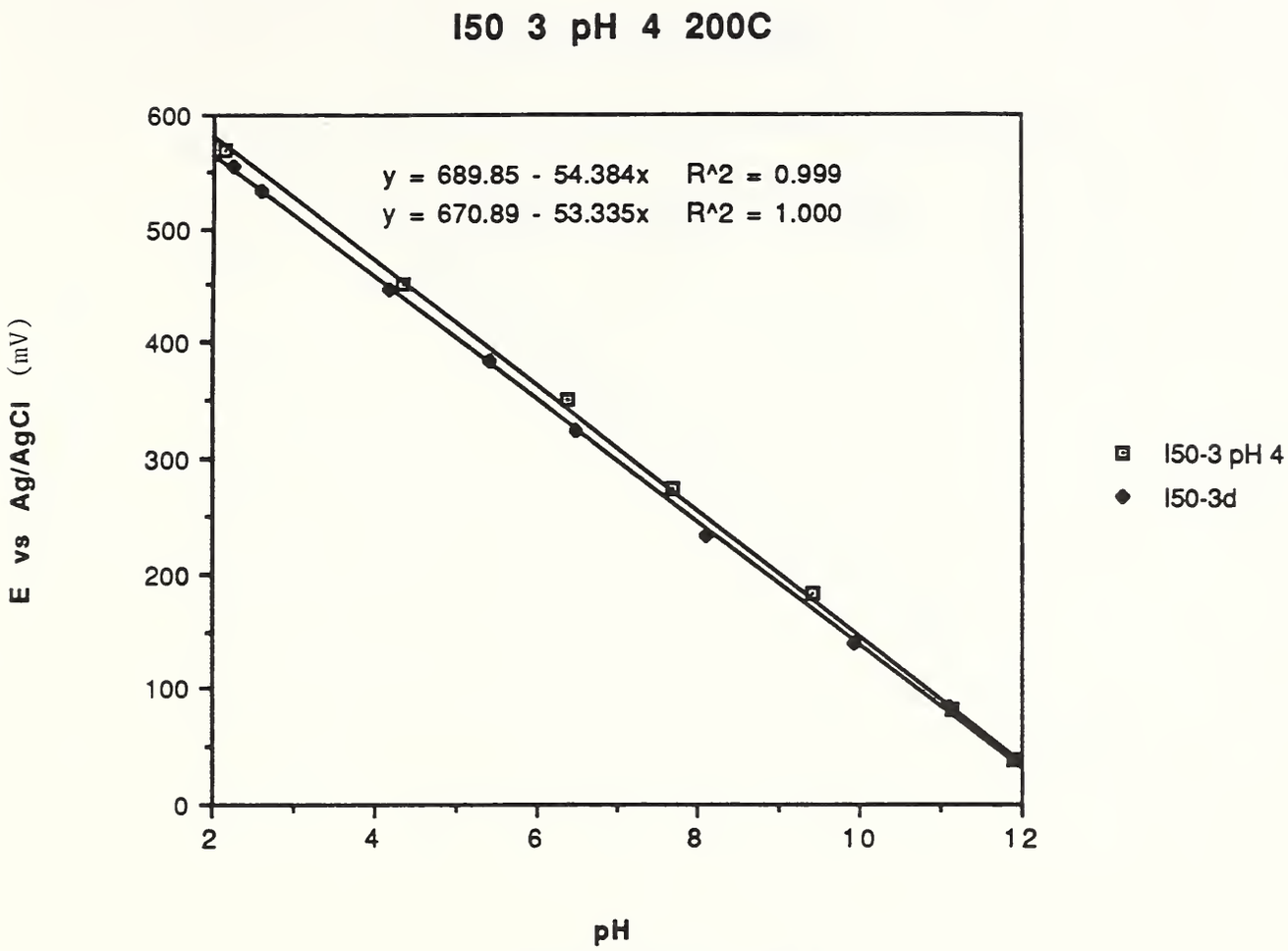


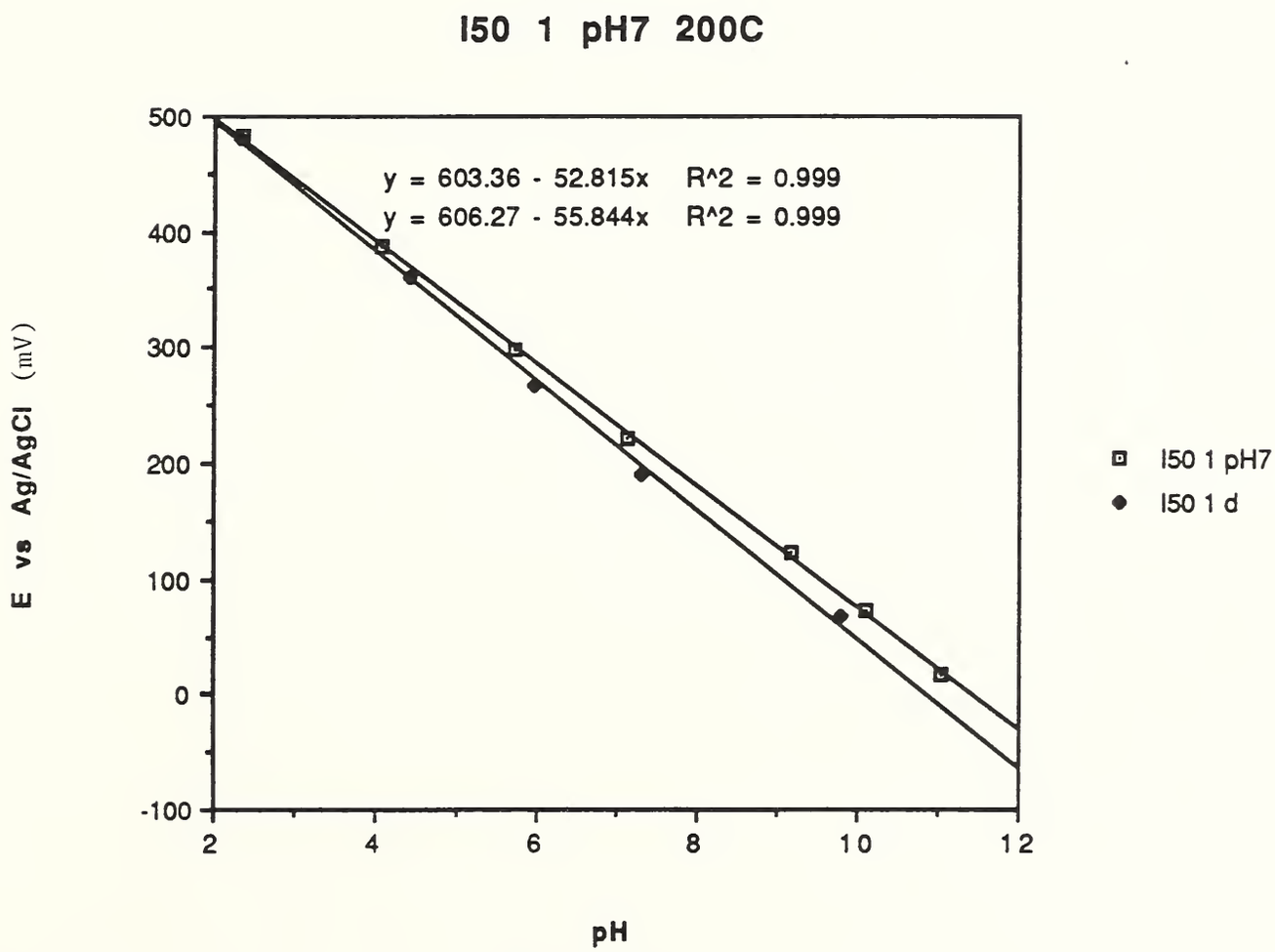
Figures 46-47



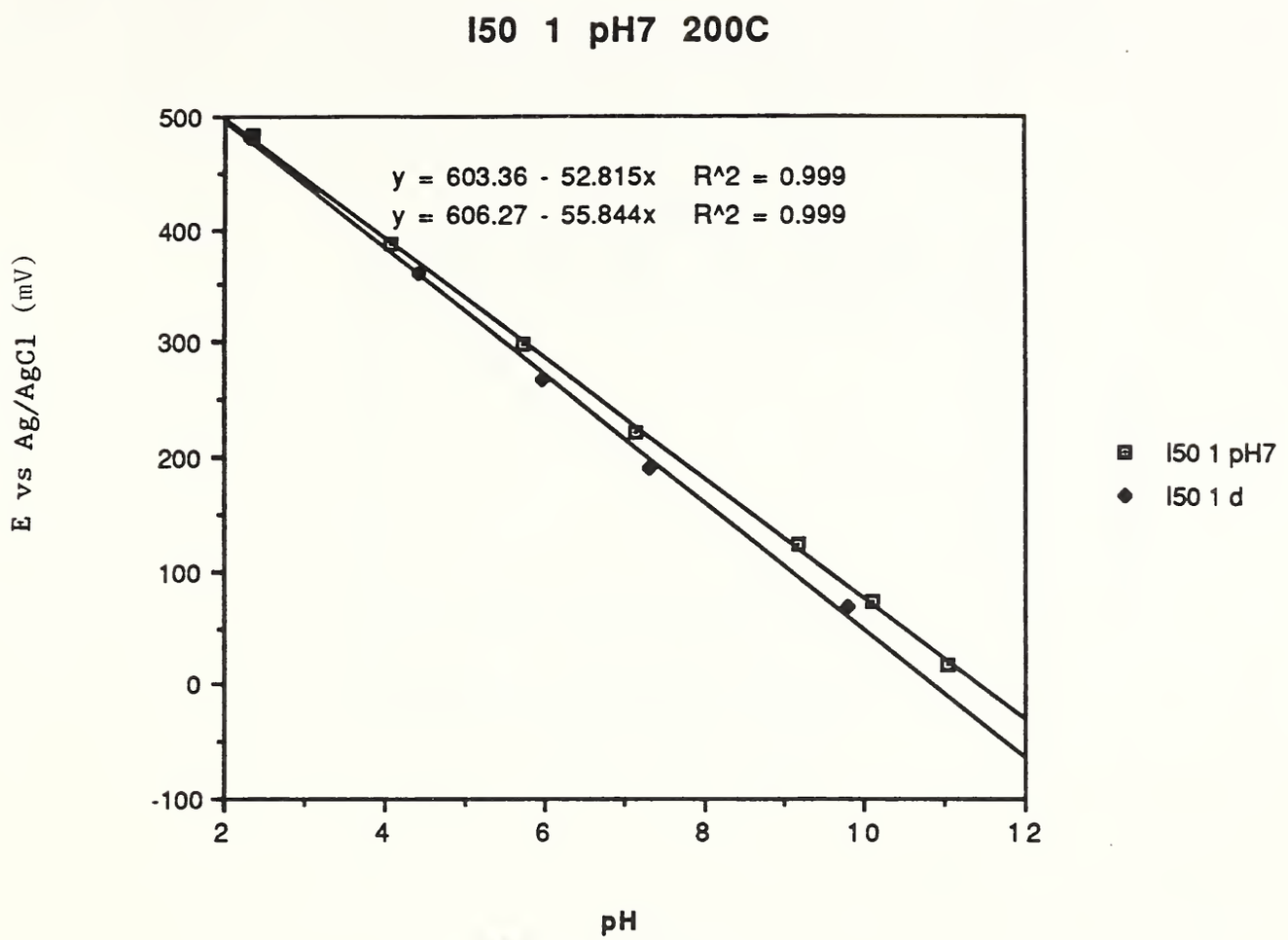


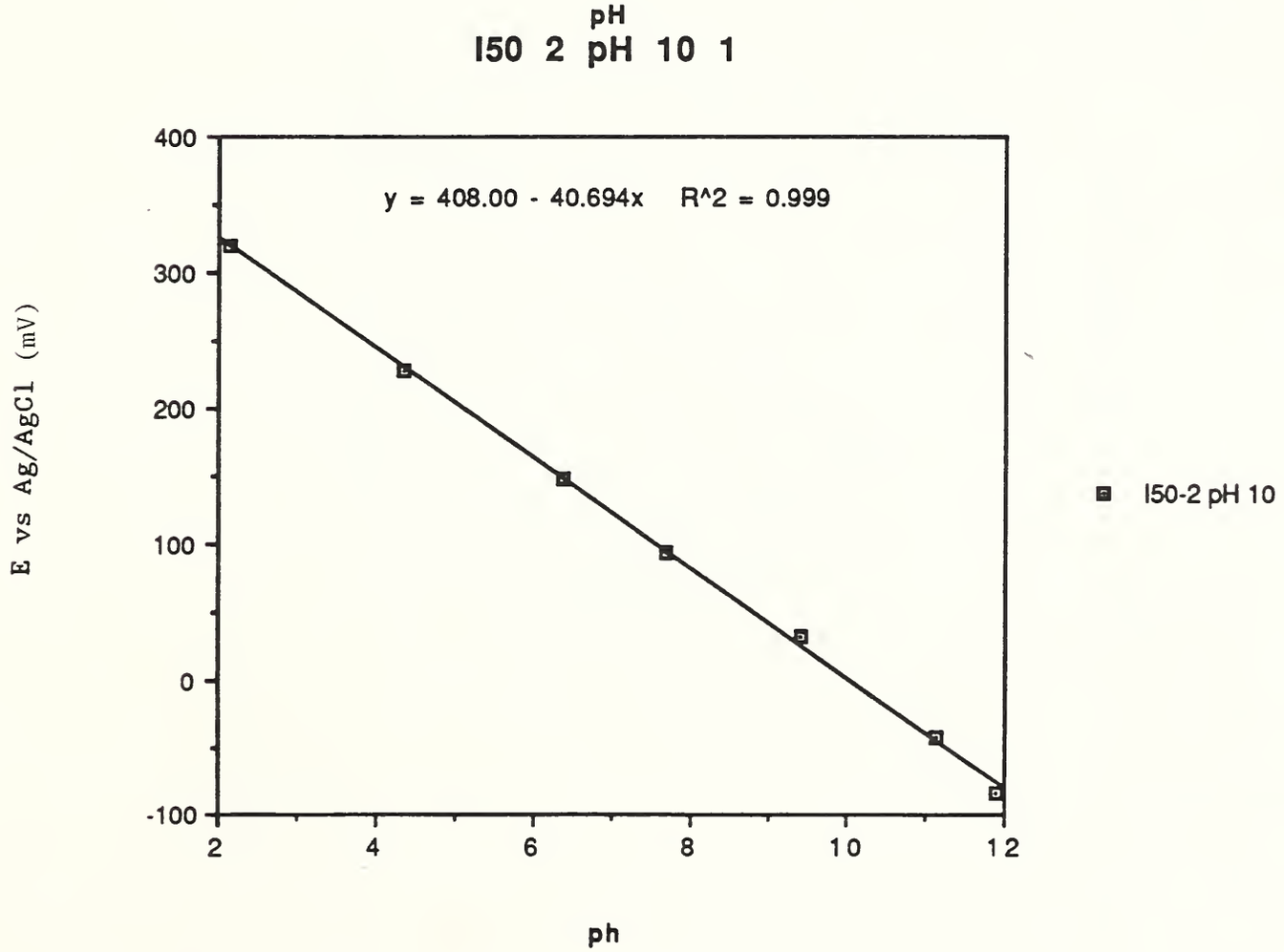
Figures 48-49



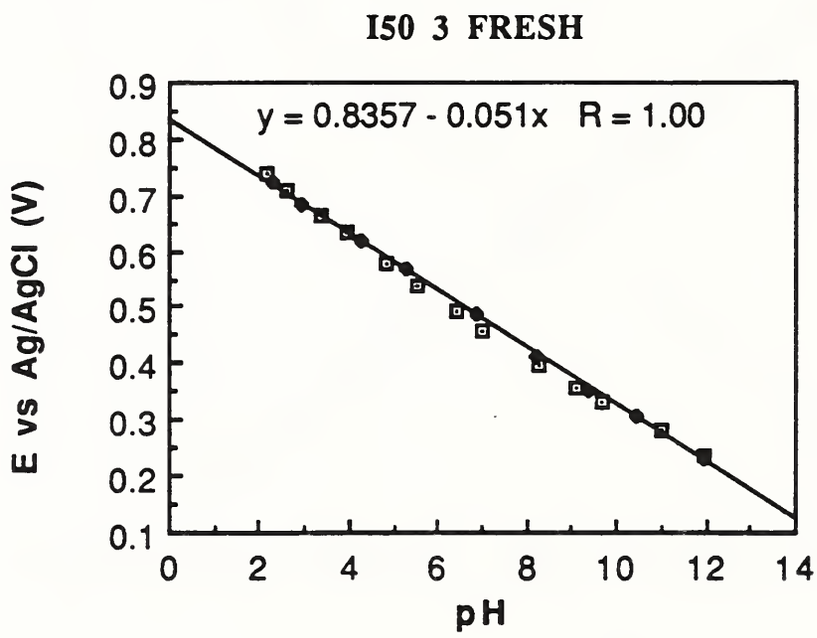


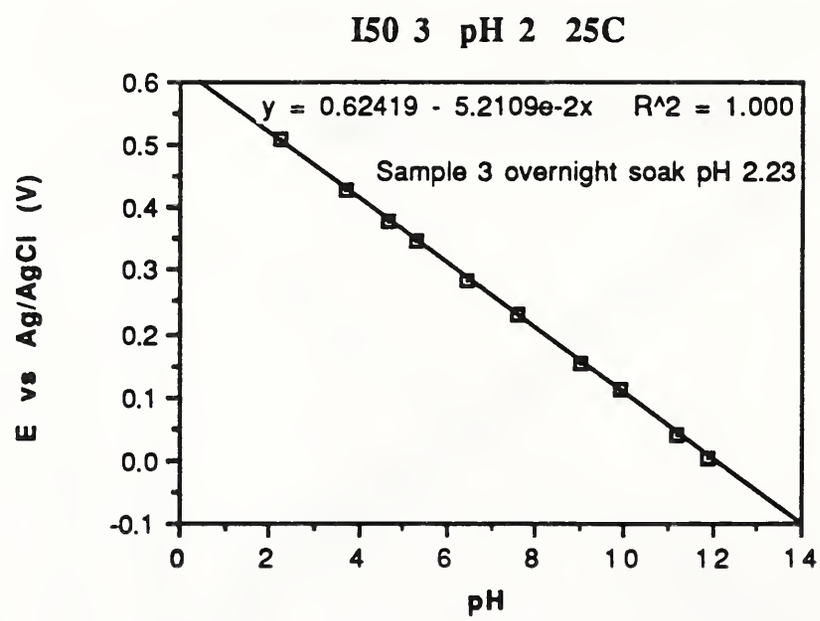
Figures 50-51



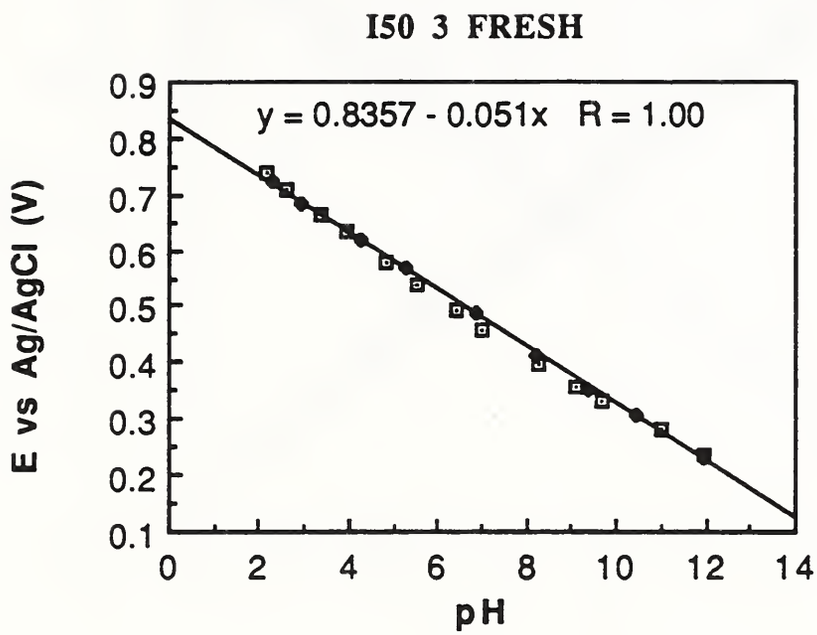


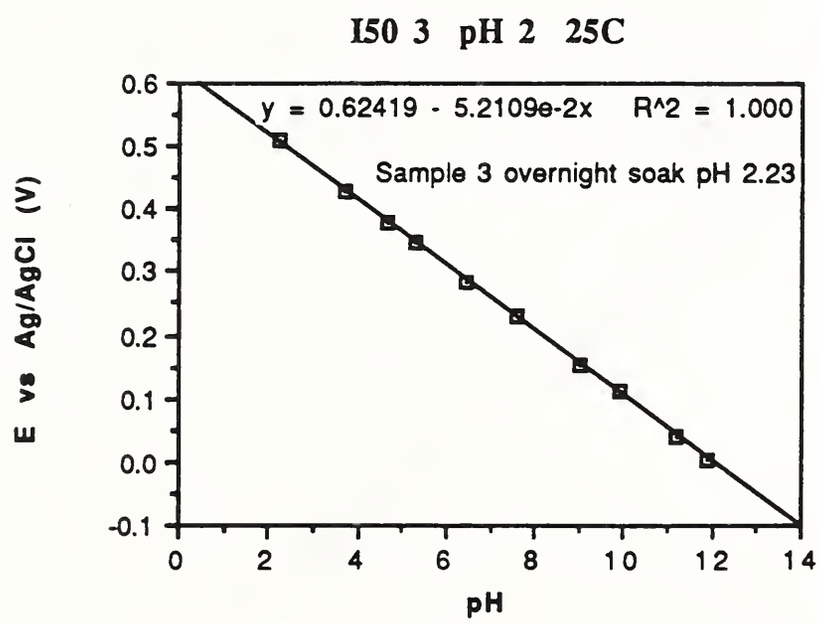
Figures 52-53



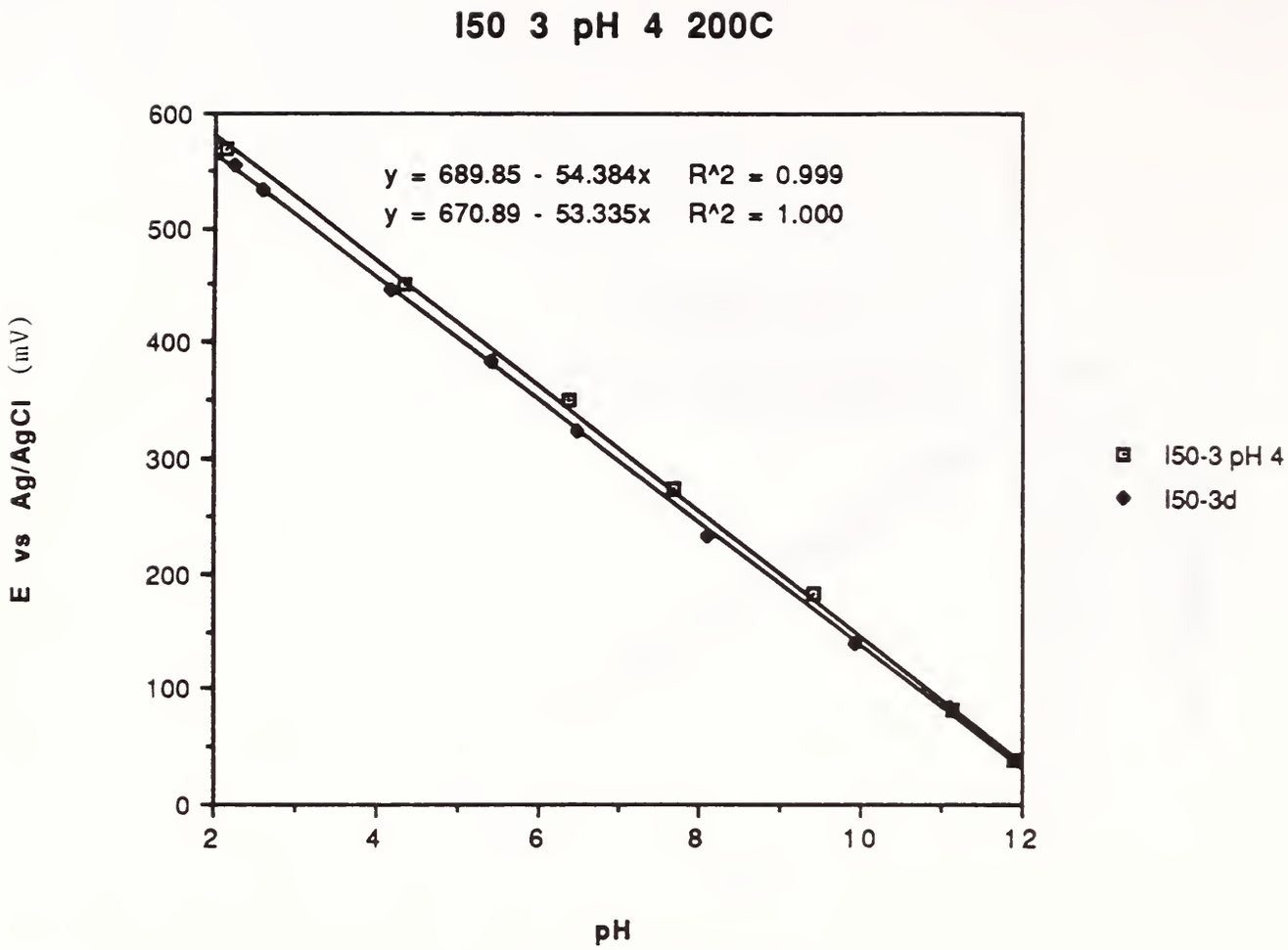


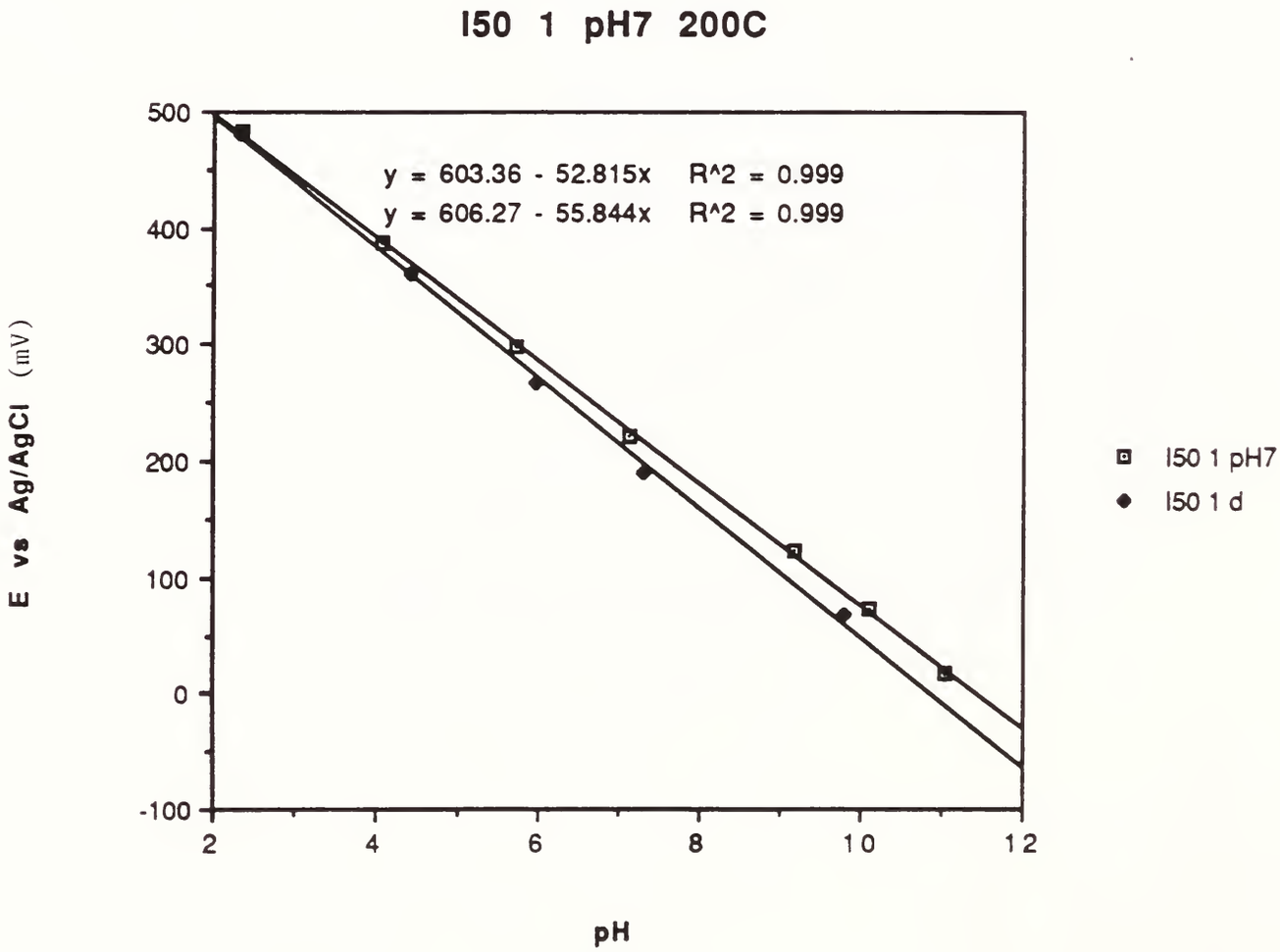
Figures 48-49



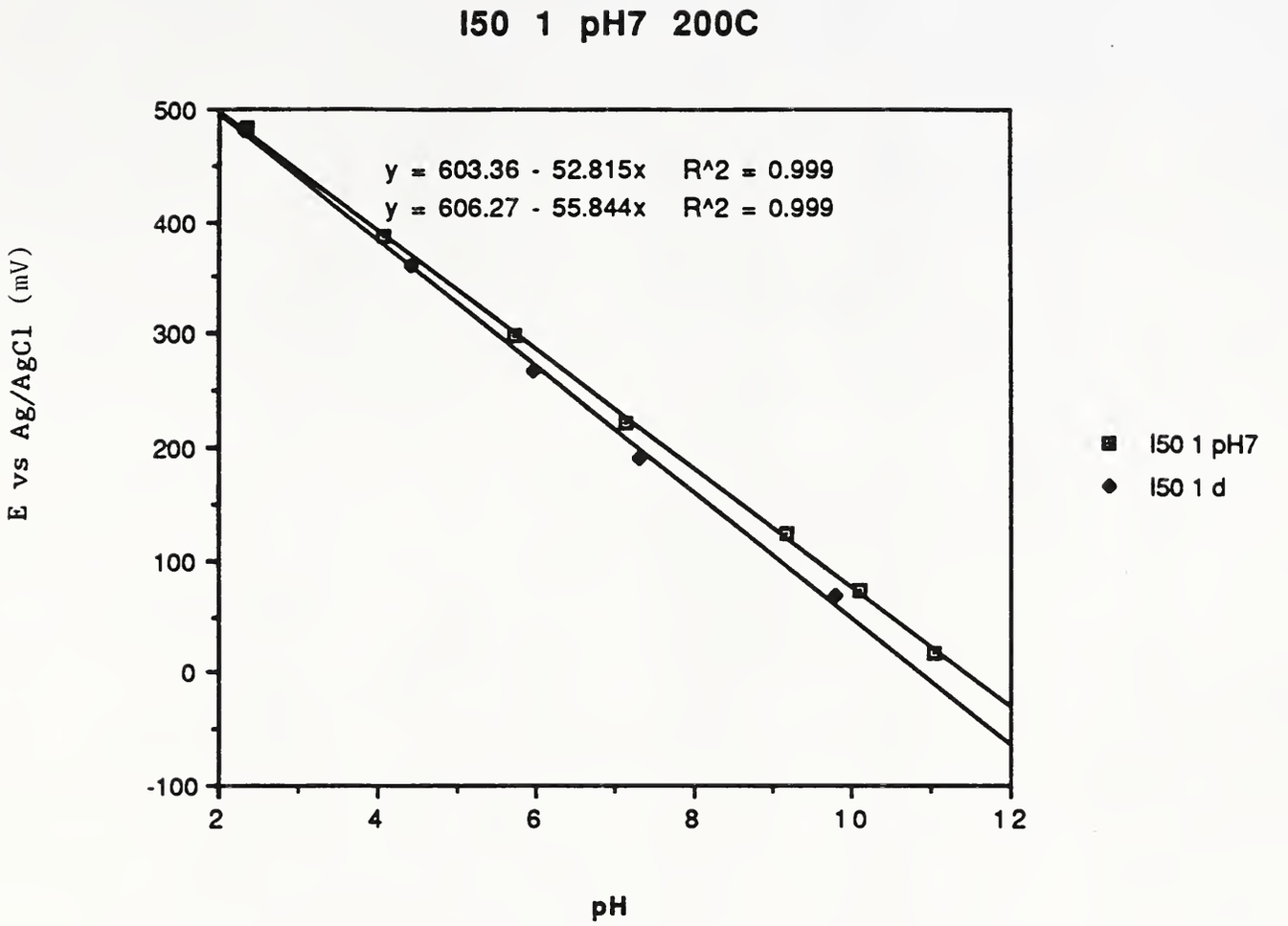


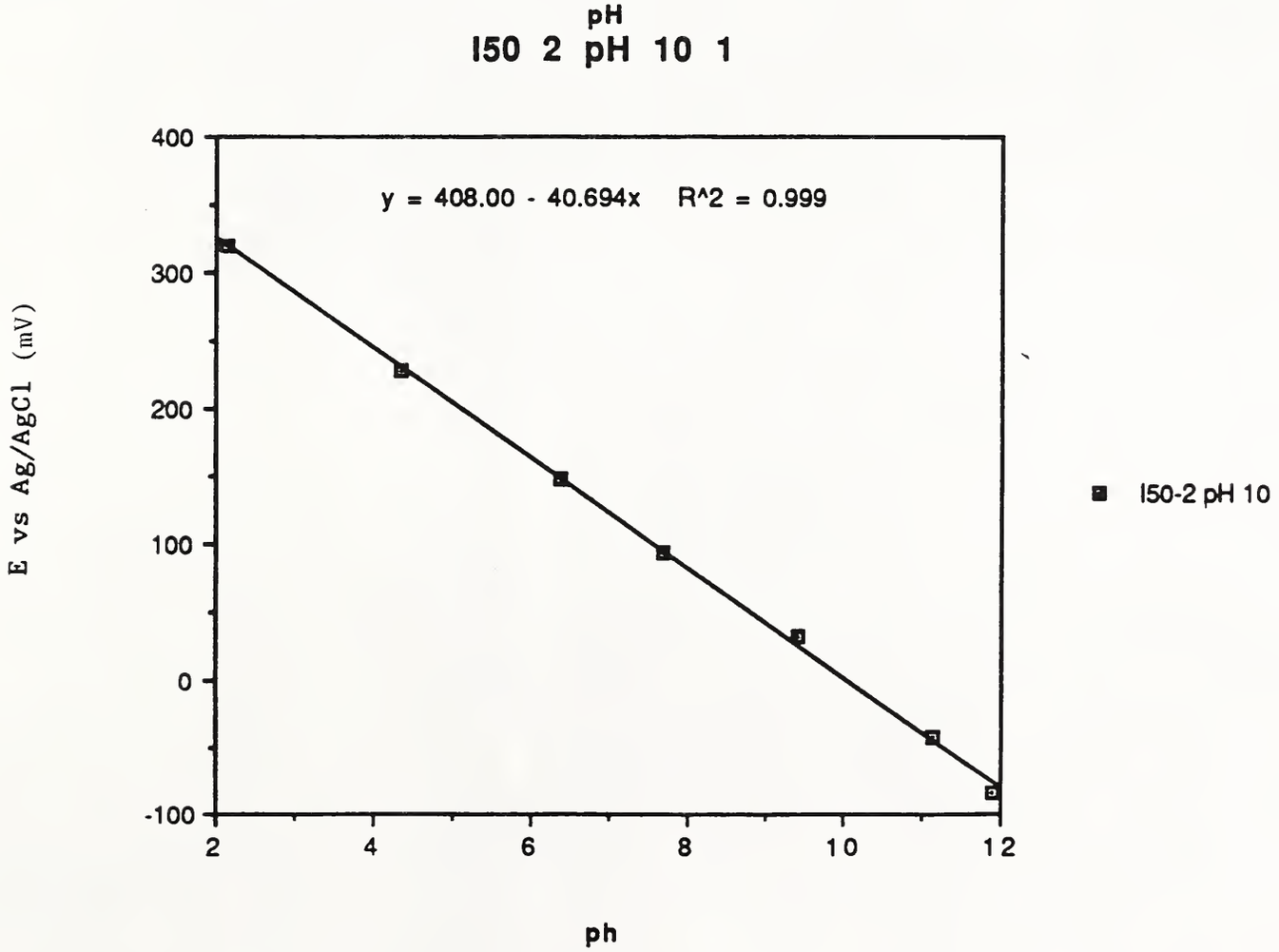
Figures 48-49





Figures 50-51





Figures 52-53