# MILLENNIUM APPLICATION BRIEF

## TOPIC: Capillary Ion Analysis (CIA) of anions, cations, organic acids and metals in nickel plating baths

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**Introduction:**

Analysis of nickel plating baths was done using a Q4000e CIA with data reduction done using the CIA option in the Millennium 2010 version 2.1 software. Analysis of anions and organic acids in a nickel plating solution was done simultaneously using either a chromate or phosphate electrolyte. Using the chromate electrolyte allows for all anions and organic acids to be resolved in less than 5 minutes. Using the phosphate electrolyte the analysis is accomplished in less than 7 minutes with a slightly improved peak shape for the citrate ion. Sulfate, however, is not detectable using the phosphate electrolyte. These two methods provide adequate analysis in a relatively fast time. Figures 1-3 are of a standard and sample, before and after plating, analyzed using the chromate electrolyte. Figures 4-6 are of a standard and another set of samples, before and after plating, analyzed using the phosphate electrolyte. Of main interest to this customer was monitoring the citrate levels during the plating process to evaluate when the citrate had depleted. By analyzing several different runs during the plating process you can get a reasonable idea when to add more material to the plating solution.

Analysis of nickel and other cations was done using the UV Cat-1 chemistries. Analysis of all cations and metals could be done in less than 5.2 minutes. In this case nickel was the ion of main interest since its depletion woud necessitate the addition of more nickel before it reached a low enough level to cause poor plating. All sample preparation for these runs was done by simply diluting and shooting. Figures 7-9 are of a cation standard and a sample before and after plating.

System suitability can also be used to build control charts for plating solutions at different sampling times during the plating process. Figures 10 and 11 are examples of a sample analyzed before plating (run 1) and at several points during the process (runs 2-4). You can further set up minimum levels allowed and have sample reports flag those runs that fall below the minimum level.

**EXPERIMENTAL:**

**Anion Analysis**

| | |
|---|---|
| System: | Q4000E |
| Electrolyte: | Chromate/OFM or Phosphate/OFM |
| Capillary: | 75um X 60cm |
| Injection: | Hydrostatic, 30 seconds |
| Run Voltage: | -20kV or -15kV |
| Detection: | Indirect UV at 254nm or Direct UV at 185nm |
| Data: | Millennium 2010 Chromatography Manager, Ver. 2.1 with CIA Option |



waters

**Cation Analysis**

| | |
|---|---|
| System: | **Q4000E** |
| Electrolyte: | UV Cat-1/HIBA |
| Capillary: | 75um X 60cm |
| Injection: | Hydrostatic, 30 seconds |
| Run Voltage: | +20kV |
| Detection: | Indirect UV at 185nm |
| Data: | **Millennium 2010 Chromatography Manager, Ver. 2.10 with CIA Option** |

**FIGURES:**

Figure 1: Electropherogram of anion/organic acid standard using chromate electrolyte
Figure 2: Electropherogram of plating solution #58 before plating using chromate electrolyte
Figure 3: Electropherogram of plating solution #58 after plating using chromate electrolyte
Figure 4: Electropherogram of anion/organic acid standard using phosphate electrolyte
Figure 5: Electropherogram of plating solution #53 before plating using phosphate electrolyte
Figure 6: Electropherogram of plating solution #53 after plating using phosphate electrolyte
Figure 7: Electropherogram of cation standard using UV Cat-1 electrolyte
Figure 8: Electropherogram of plating solution #53 before plating using UV Cat-1 electrolyte
Figure 9: Electropherogram of plating solution #53 after plating using UV Cat-1 electrolyte
Figure 10: Control chart for organic acids and chloride from a sample before and during the plating process
Figure 10: Summary Bar chart for organic acids and chloride from a sample before and during the plating process

Millennium Results Report: CIA_Anions Proc Chan: SATIN Page 1

For Sample: Std2 Vial: 2 Inj: 2 Chan: SATIN Date Processed 11/30/94 04:14:23 PM

Channel Descr: Indirect UV

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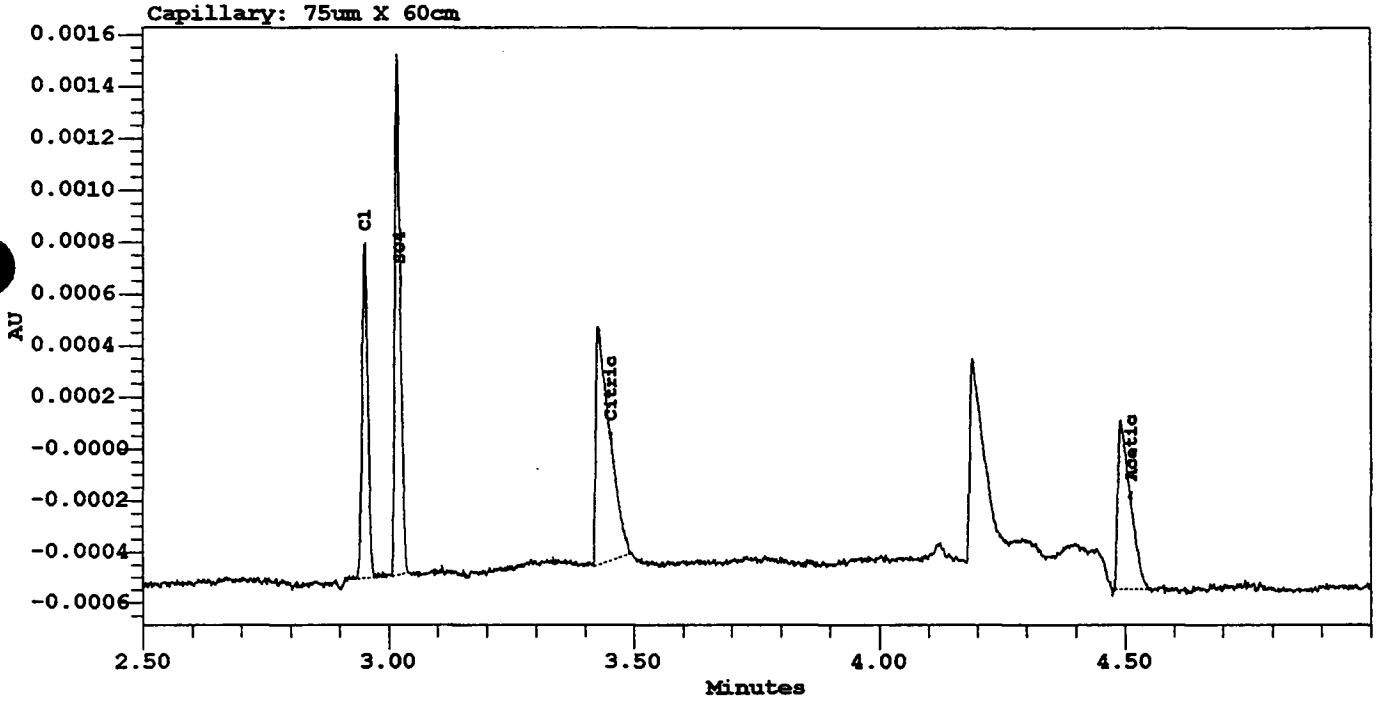
Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | Std2 | | |
| Vial: | 2 | Sample Type: | Standard |
| Injection: | 2 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 5.0 min |
| Date Acquired: | 11/30/94 03:33:07 PM | Date Processed: | 11/30/94 04:14:23 PM |
| Scale Factor: | 1.00 | Dilution: | 1.00000 |
| Acq Meth Set: | CIA_Anion01 | | |
| Processing Method: | Plating_Anions01 | | |

SampleName: Std2 Electrolyte: 4.0 mM Chromate/0.5 mM OFM RunVoltage: -20kV
Detection: Indirect 254nm, 0.1 TC InjectionMode: Hydrostatic, 30sec
Capillary: 75um X 60cm




*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | Cl | 2.952 | 1028 | 1308 | 2.000 |
| 2 | SO4 | 3.024 | 1531 | 2016 | 4.000 |
| 3 | Citric | 3.455 | 1826 | 925 | 6.000 |
| 4 | Acetic | 4.513 | 1172 | 655 | 2.000 |

fig. 1

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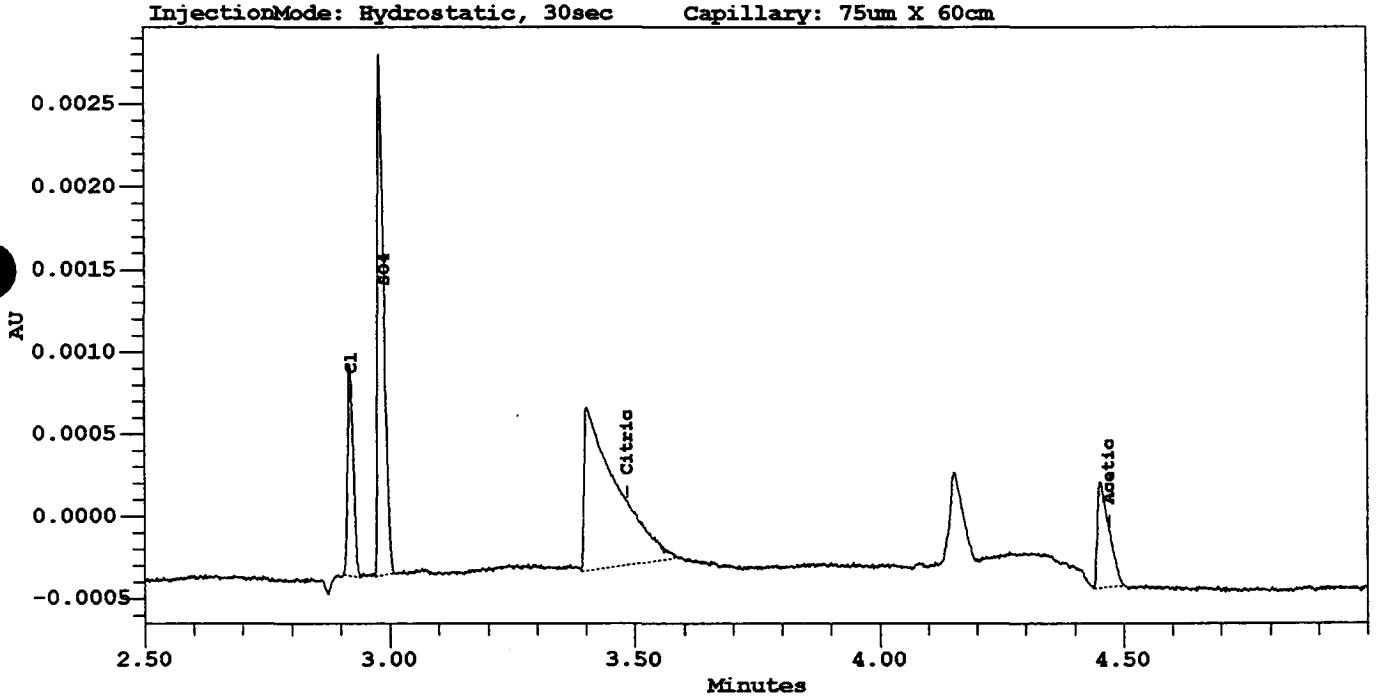
## Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | 58 Before (0.02-100mL) | | |
| Vial: | 4 | Sample Type: | Unknown |
| Injection: | 2 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 5.0 min |
| Date Acquired: | 11/30/94 04:05:42 PM | Date Processed: | 11/30/94 04:14:42 PM |
| Scale Factor: | 1.00 | Dilution: | 5000.00000 |
| Acq Meth Set: | CIA_Anion01 | | |
| Processing Method: | Plating_Anions01 | | |

**SampleName: 58 Before (0.02-100mL) Electrolyte: 4.0 mM Chromate/0.5 mM OFM**
**RunVoltage: -20kV Detection: Indirect 254nm, 0.1 TC**
**InjectionMode: Hydrostatic, 30sec Capillary: 75um X 60cm**




*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | Cl | 2.923 | 1008 | 1291 | 9792.928 |
| 2 | SO4 | 2.990 | 2816 | 3190 | 36993.650 |
| 3 | Citric | 3.486 | 4557 | 990 | 70253.175 |
| 4 | Acetic | 4.471 | 1060 | 651 | 9342.332 |

Fig. 2

Millennium Results Report: CIA_Anions Proc Chan: SATIN Page 1

For Sample: 58 After (0.02- Vial: 5 Inj: 2 Chan: SATIN Date Processed 11/30/94 04:28:09 PM

Channel Descr: Indirect UV

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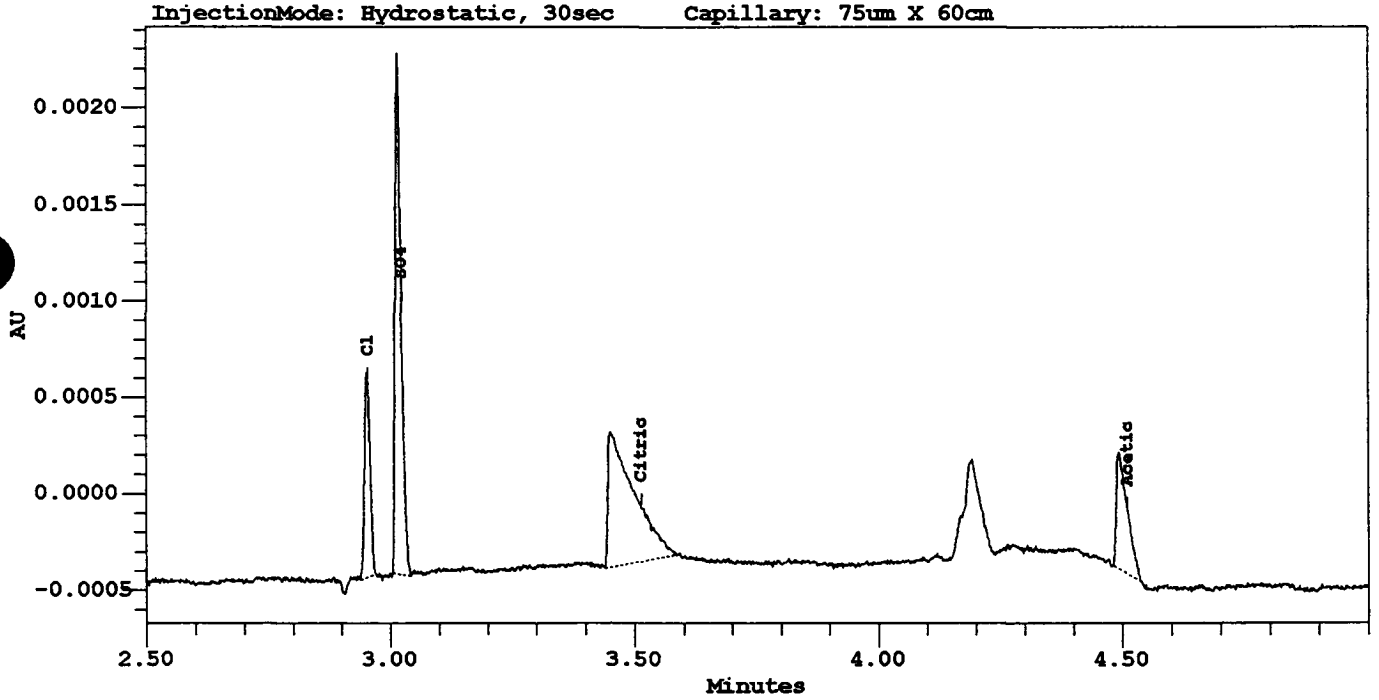
Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | 58 After (0.02-100mL) | | |
| Vial: | 5 | Sample Type: | Unknown |
| Injection: | 2 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 5.0 min |
| Date Acquired: | 11/30/94 04:21:05 PM | Date Processed: | 11/30/94 04:28:09 PM |
| Scale Factor: | 1.00 | Dilution: | 5000.00000 |
| Acq Meth Set: | CIA_Anion01 | | |
| Processing Method: | Plating_Anions01 | | |

SampleName: 58 After (0.02-100mL) Electrolyte: 4.0 mM Chromate/0.5 mM OFM
RunVoltage: -20kV Detection: Indirect 254nm, 0.1 TC
InjectionMode: Hydrostatic, 30sec Capillary: 75um X 60cm




*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | Cl | 2.955 | 824 | 1066 | 7771.317 |
| 2 | SO4 | 3.024 | 2257 | 2724 | 29370.631 |
| 3 | Citric | 3.514 | 2571 | 700 | 40633.495 |
| 4 | Acetic | 4.511 | 956 | 610 | 8361.688 |

fig. 3

Millennium Results Report: CIA_Anions_P01 Proc Chan: SATIN Page 1

For Sample: Std2 Vial: 3 Inj: 1 Chan: SATIN Date Processed 12/02/94 12:29:56 PM

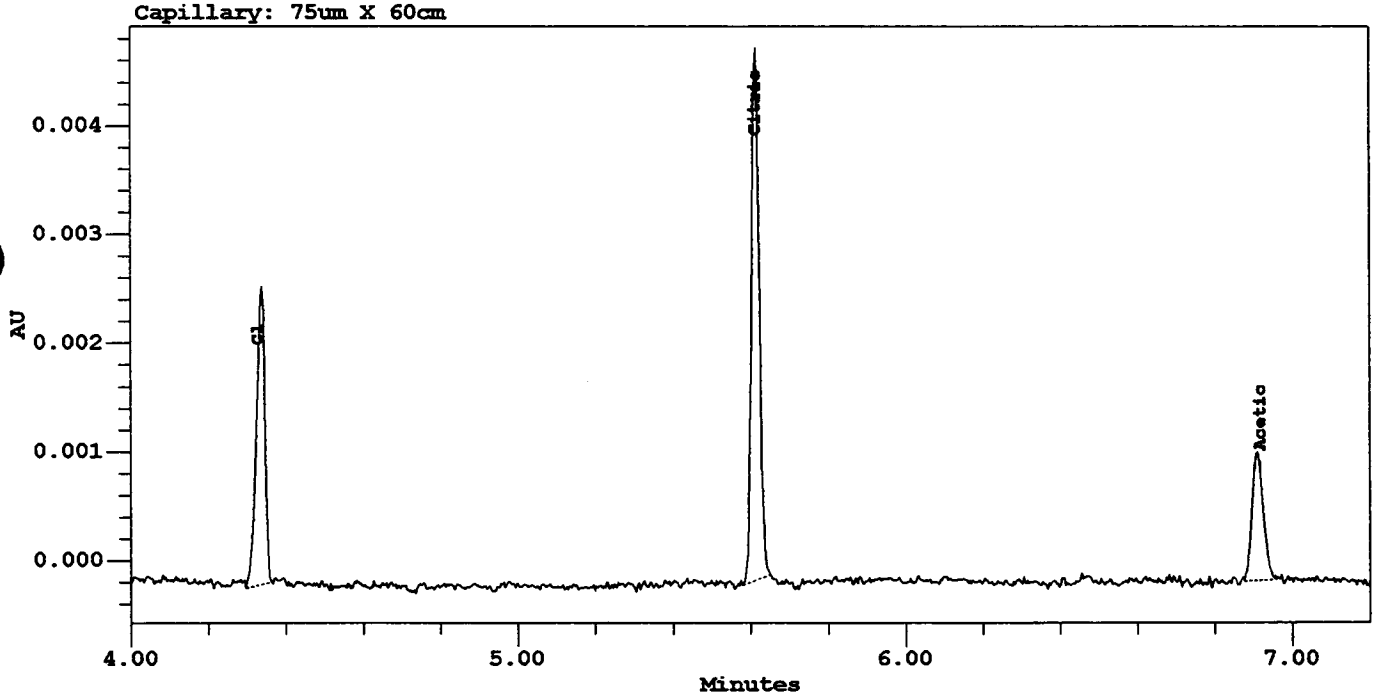
Channel Descr: Indirect UV

N o r t h e r n K e n t u c k y L a b o r a t o r y

S a m p l e I n f o r m a t i o n

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | Std2 | | |
| Vial: | 3 | Sample Type: | Standard |
| Injection: | 1 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 7.2 min |
| Date Acquired: | 12/02/94 11:45:44 AM | Date Processed: | 12/02/94 12:29:56 PM |
| Scale Factor: | 1.00 | Dilution: | 1.00000 |
| Acq Meth Set: | CIA_Anion_5pts | | |
| Processing Method: | Plating_Phosphate01 | | |

**SampleName: Std2 Electrolyte: 25 mm Phosphate/0.5 mM OFM-OH RunVoltage: -15kV**
**Detection: Direct 185nm, 0.1 TC InjectionMode: Hydrostatic, 30sec**
**Capillary: 75um X 60cm**




*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | Cl | 4.330 | 4125 | 2737 | 2.000 |
| 2 | Citric | 5.615 | 6563 | 4851 | 6.000 |
| 3 | Acetic | 6.918 | 2411 | 1182 | 2.000 |

fig. 4

Millennium Results Report: CIA_Anions_P01 Proc Chan: SATIN Page 1

For Sample: 53 Before (0.02 Vial: 6 Inj: 1 Chan: SATIN Date Processed 12/02/94 12:38:20 PM

Channel Descr: Indirect UV

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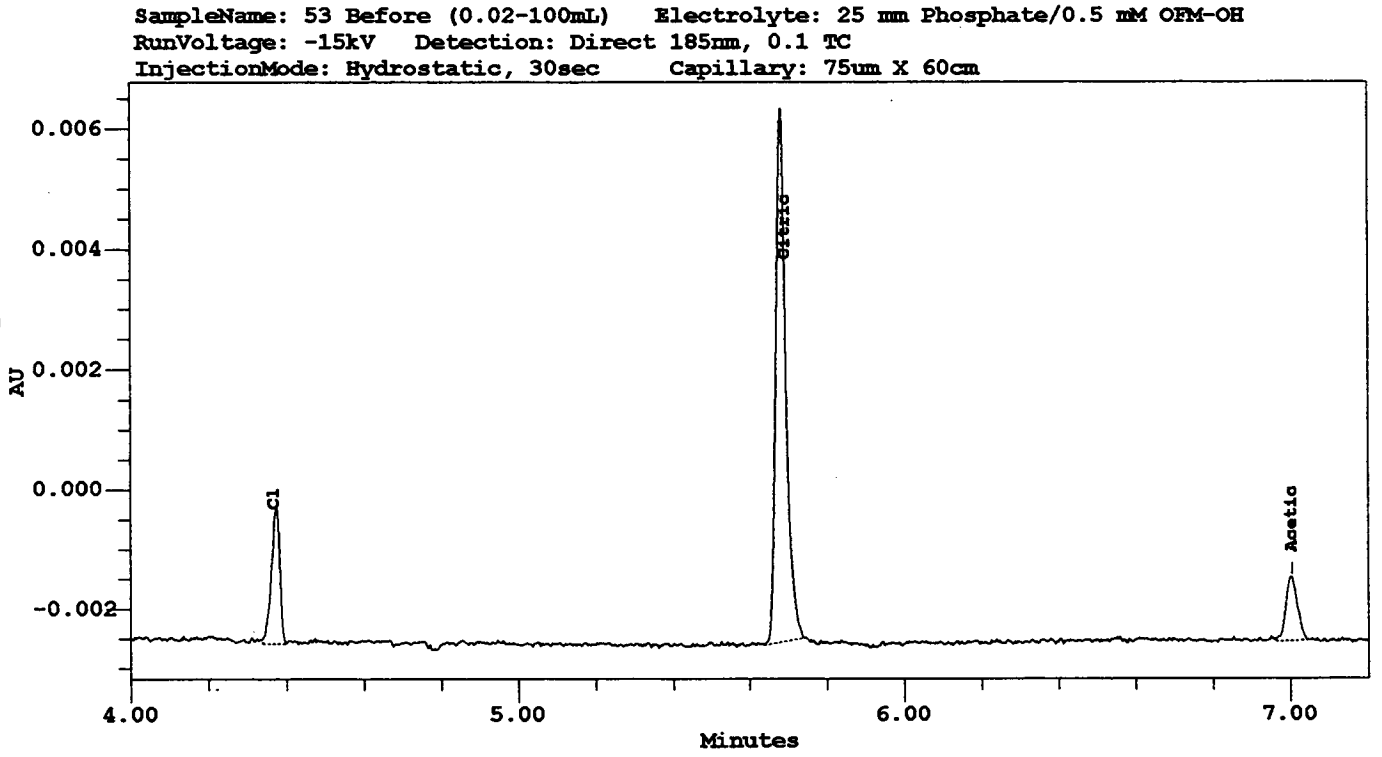
Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | 53 Before (0.02-100mL) | | |
| Vial: | 6 | Sample Type: | Unknown |
| Injection: | 1 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 7.2 min |
| Date Acquired: | 12/02/94 12:25:20 PM | Date Processed: | 12/02/94 12:38:20 PM |
| Scale Factor: | 1.00 | Dilution: | 5000.00000 |
| Acq Meth Set: | CIA_Anion_5pts | | |
| Processing Method: | Plating_Phosphate01 | | |




*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | Cl | 4.367 | 3446 | 2311 | 8457.296 |
| 2 | Citric | 5.692 | 16248 | 8887 | 73017.185 |
| 3 | Acetic | 7.005 | 2262 | 1073 | 9171.118 |

fig. 5

For Sample: 53 After (0.02- Vial: 7 Inj: 1 Chan: SATIN Date Processed 12/02/94 12:57:47 PM

Channel Descr: Indirect UV

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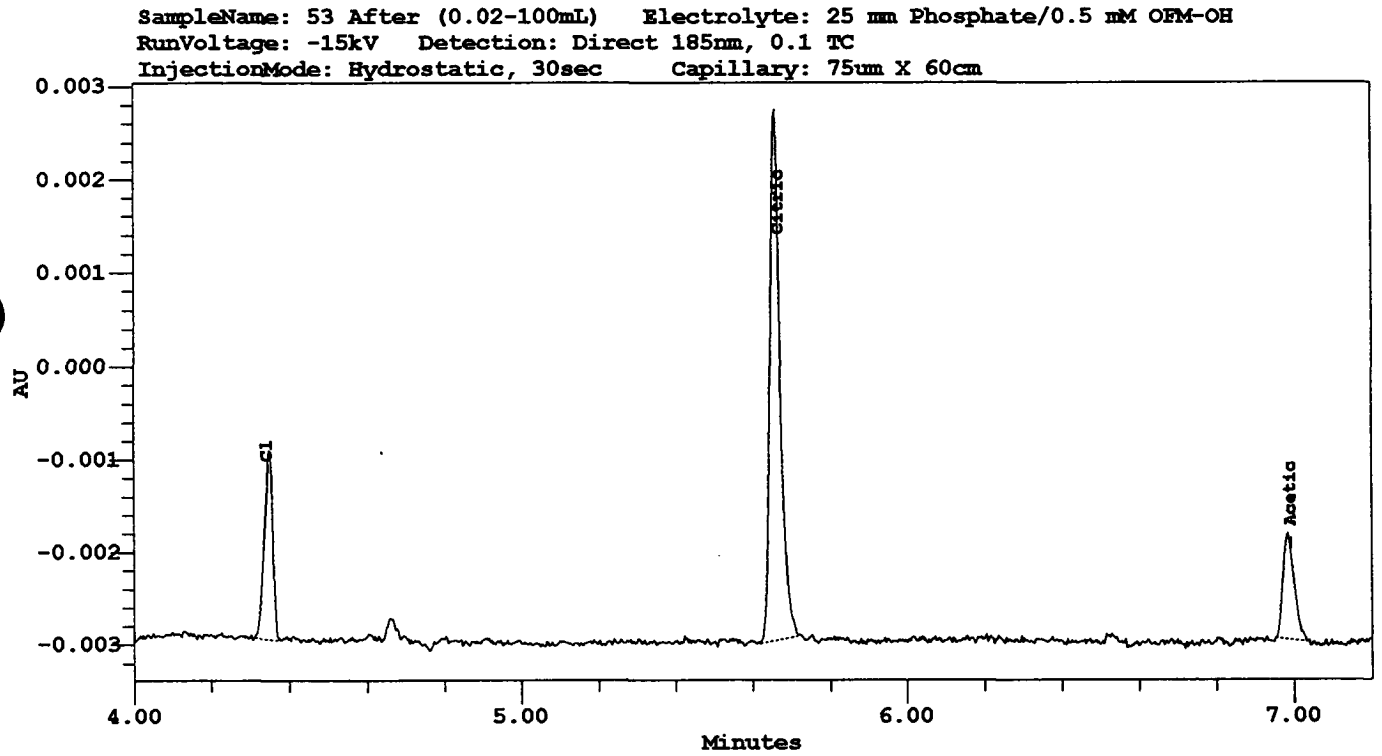
## Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | 53 After (0.02-100mL) | | |
| Vial: | 7 | Sample Type: | Unknown |
| Injection: | 1 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 7.2 min |
| Date Acquired: | 12/02/94 12:35:14 PM | Date Processed: | 12/02/94 12:57:47 PM |
| Scale Factor: | 1.00 | Dilution: | 5000.00000 |
| Acq Meth Set: | CIA_Anion_5pts | | |
| Processing Method: | Plating_Phosphate01 | | |




*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | Cl | 4.343 | 2964 | 2052 | 7312.004 |
| 2 | Citric | 5.668 | 10488 | 5705 | 47434.357 |
| 3 | Acetic | 6.993 | 2309 | 1149 | 9366.215 |

fig. 6

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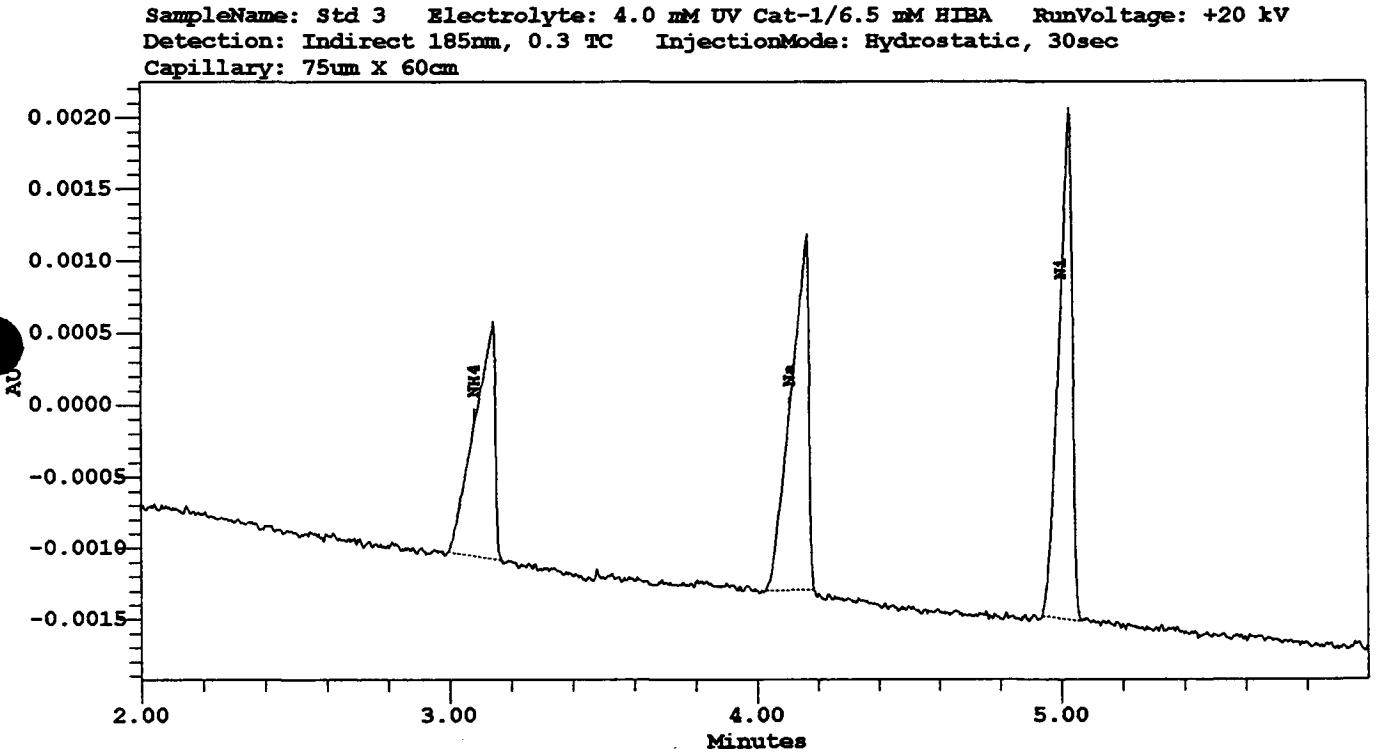
Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | Std 3 | | |
| Vial: | 5 | Sample Type: | Standard |
| Injection: | 2 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 7.0 min |
| Date Acquired: | 11/28/94 12:56:20 PM | Date Processed: | 11/30/94 05:41:31 PM |
| Scale Factor: | 1.00 | Dilution: | 1.00000 |
| Acq Meth Set: | CIA_01 | | |
| Processing Method: | Plating_Cations_02a | | |



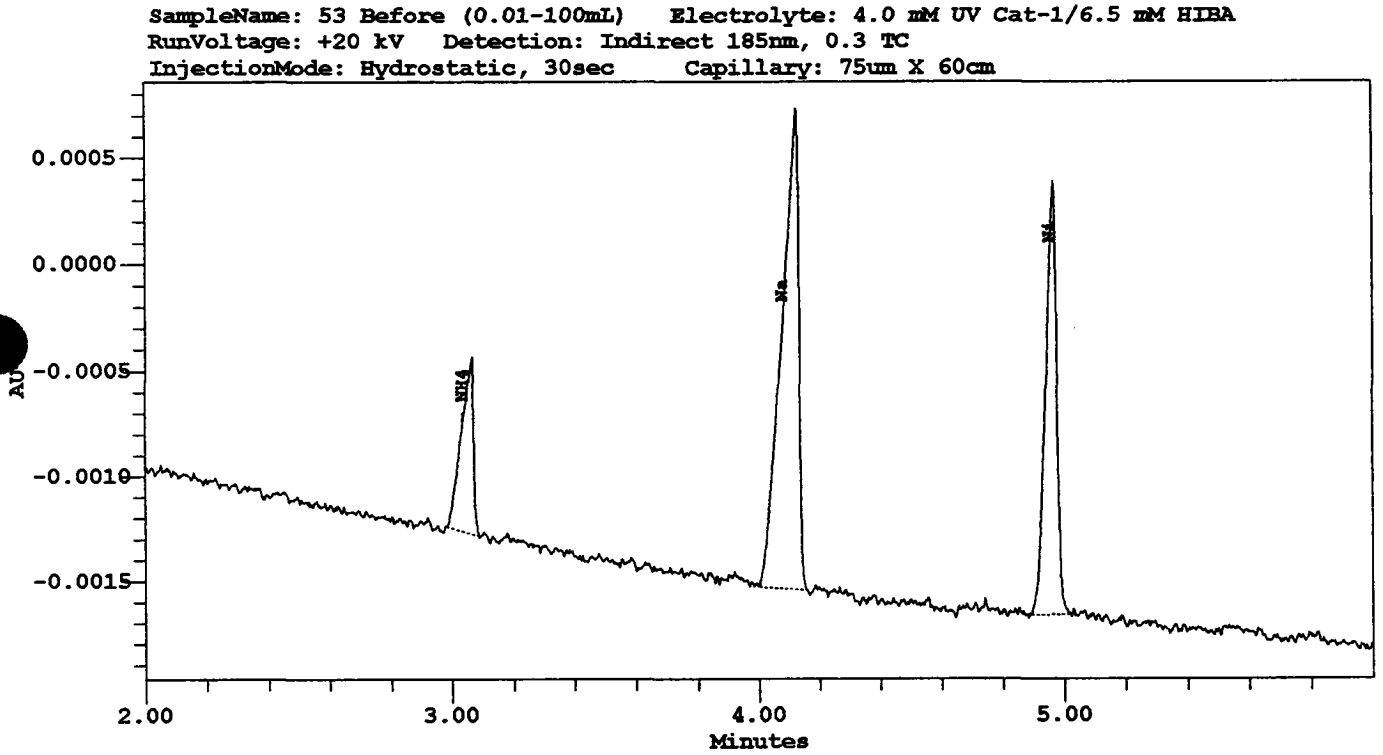

*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | NH4 | 3.082 | 7728 | 1657 | 4.000 |
| 2 | Na | 4.108 | 10004 | 2480 | 4.000 |
| 3 | Ni | 5.000 | 10901 | 3570 | 6.000 |

fig. 7

# Northern Kentucky Laboratory
## Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | 53 Before (0.01-100mL) | | |
| Vial: | 6 | Sample Type: | Unknown |
| Injection: | 1 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 7.0 min |
| Date Acquired: | 11/28/94 01:05:33 PM | Date Processed: | 11/30/94 05:42:22 PM |
| Scale Factor: | 1.00 | Dilution: | 10000.00000 |
| Acq Meth Set: | CIA_01 | | |
| Processing Method: | Plating_Cations_02a | | |




*Peak Results*

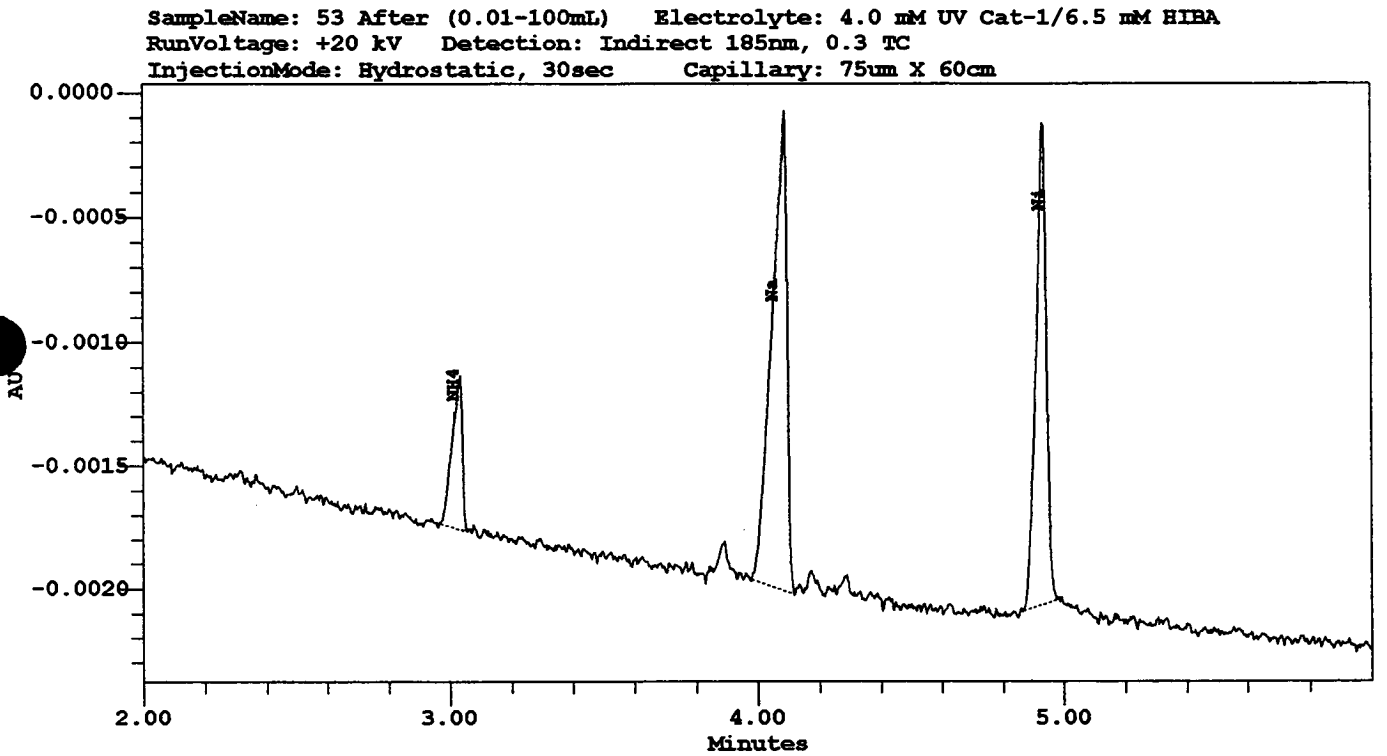
| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | NH4 | 3.035 | 2267 | 839 | 12008.021 |
| 2 | Na | 4.080 | 8715 | 2273 | 34760.459 |
| 3 | Ni | 4.953 | 5227 | 2052 | 29785.775 |

Fig. 8

For Sample: 53 After (0.01- Vial: 8 Inj: 1 Chan: SATIN Date Processed 11/30/94 05:47:00 PM
Channel Descr: Indirect UV

Northern Kentucky Laboratory
Sample Information

| | | | |
|---|---|---|---|
| Project Name: | CIA_Plating01 | | |
| SampleName: | 53 After (0.01-100mL) | | |
| Vial: | 8 | Sample Type: | Unknown |
| Injection: | 1 | Volume: | 30.00 |
| Channel: | SATIN | Run Time: | 7.0 min |
| Date Acquired: | 11/28/94 01:42:20 PM | Date Processed: | 11/30/94 05:47:00 PM |
| Scale Factor: | 1.00 | Dilution: | 10000.00000 |
| Acq Meth Set: | CIA_01 | | |
| Processing Method: | Plating_Cations_02a | | |



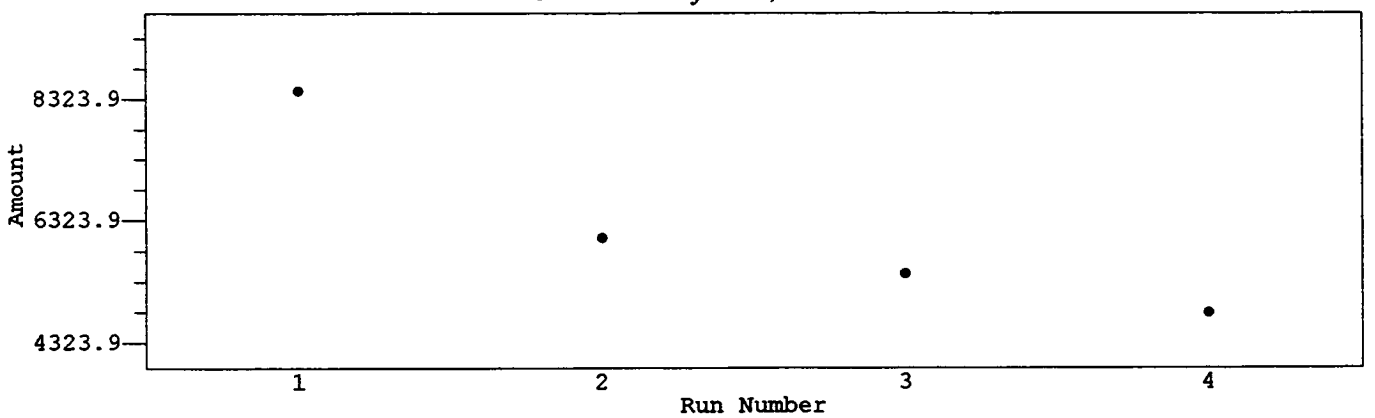

*Peak Results*

| # | Name | Migration Time (min) | Area (uV*sec) | Height (uV) | Amount-ppm |
|---|---|---|---|---|---|
| 1 | NH4 | 3.013 | 1402 | 628 | 7482.546 |
| 2 | Na | 4.050 | 6436 | 1938 | 25861.046 |
| 3 | Ni | 4.922 | 4687 | 1942 | 26876.732 |

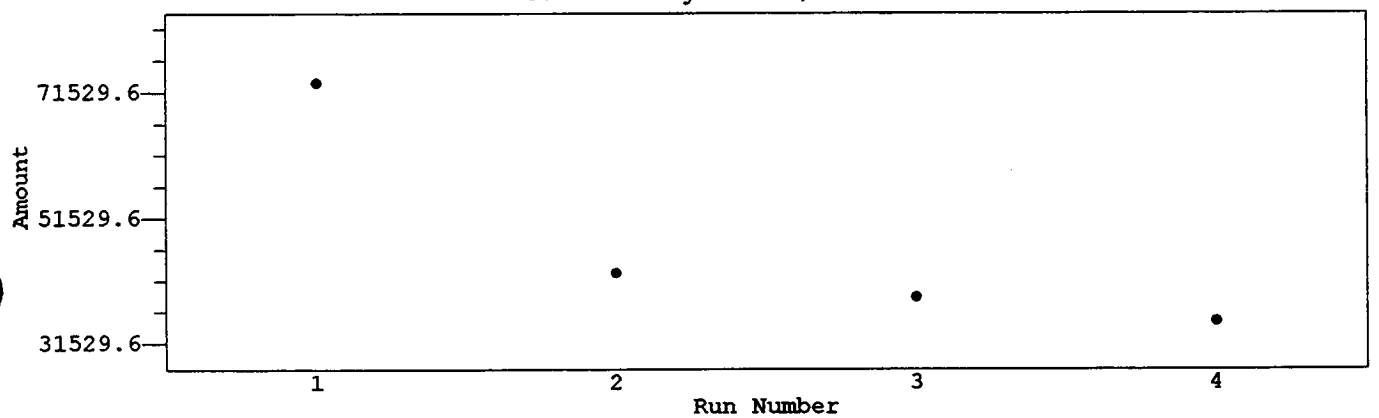
fig. 9

Project Name: CIA_Plating01 Username: Stuart
Date Prepared: December 2, 1994

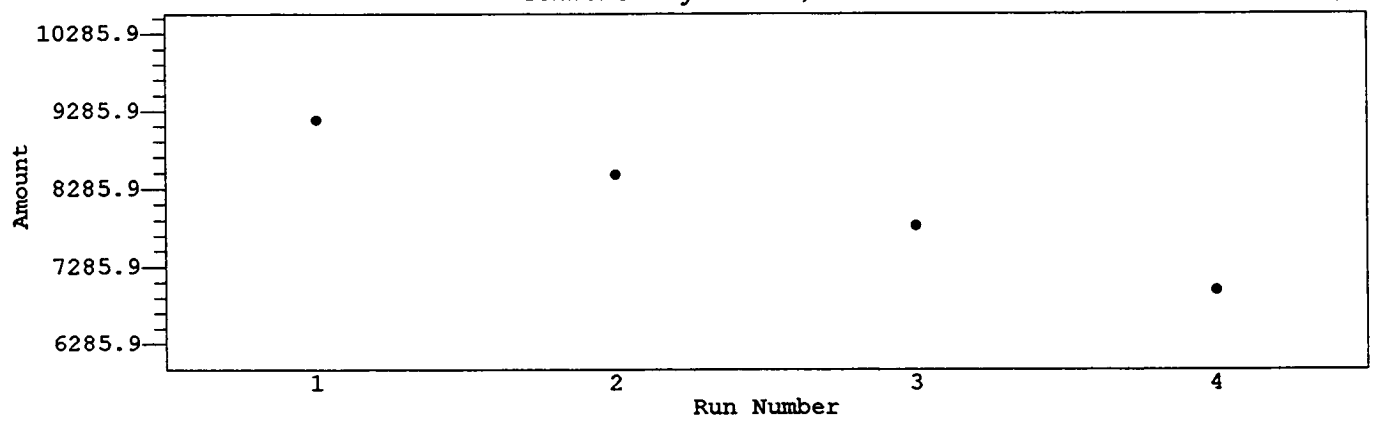
*Control Chart for: Cl, Channel: SATIN*




*Control Chart for: Citric, Channel: SATIN*




*Control Chart for: Acetic, Channel: SATIN*



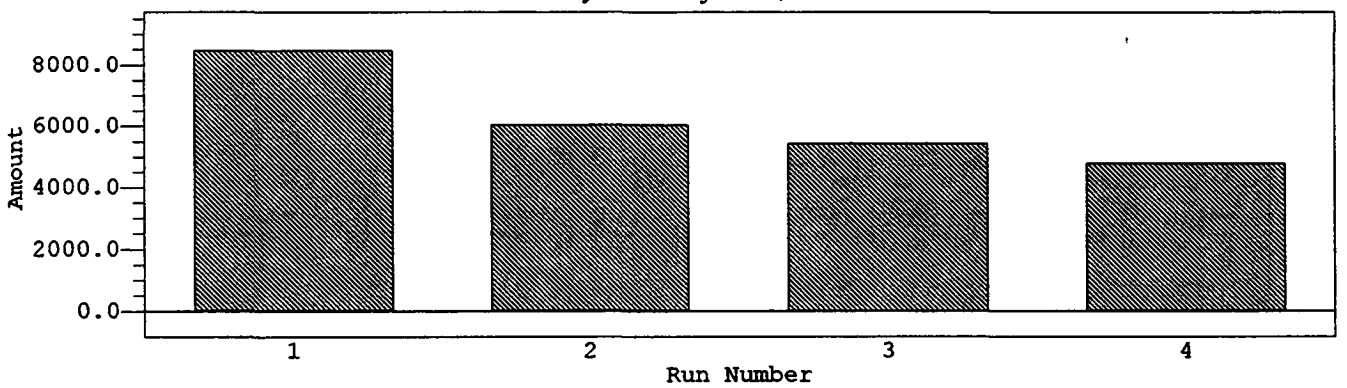

*Run ID*

| # | SampleName | Dilution |
|---|---|---|
| 1 | 53 Before (0.02-100mL) | 5000.00000 |
| 2 | 53 After#1 (0.02-100mL) | 5000.00000 |
| 3 | 53 After#2 (0.02-100mL) | 5000.00000 |
| 4 | 53 After#3 (0.02-100mL) | 5000.00000 |

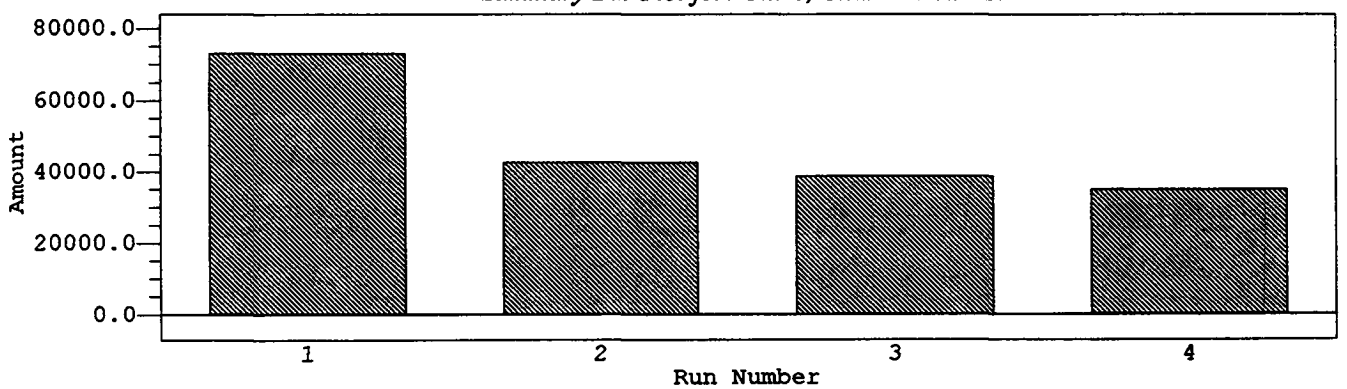
fig. 10

Project Name: CIA_Plating01 Username: Stuart
Date Prepared: December 2, 1994

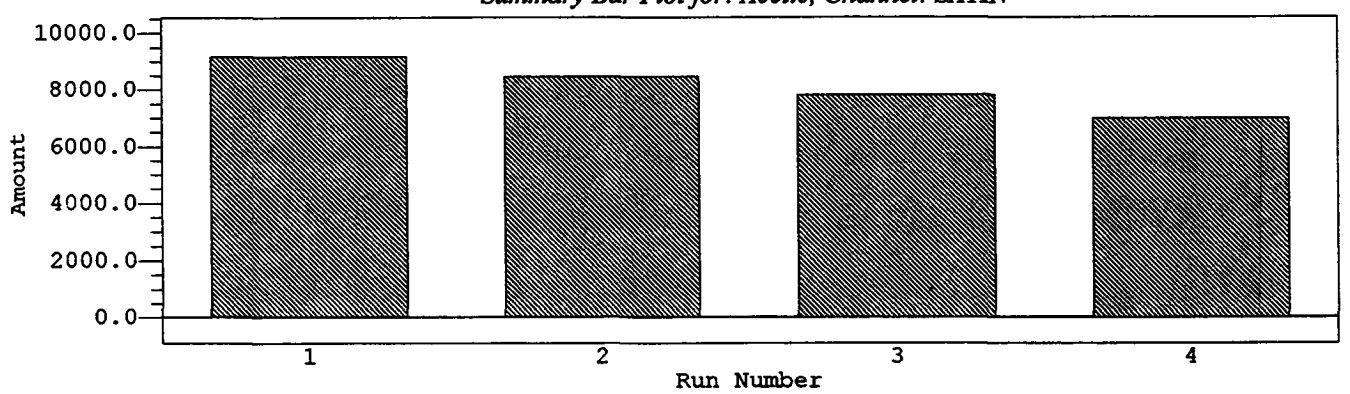
*Summary Bar Plot for: Cl, Channel: SATIN*




*Summary Bar Plot for: Citric, Channel: SATIN*




*Summary Bar Plot for: Acetic, Channel: SATIN*




*Run ID*

| # | SampleName | Dilution |
|---|---|---|
| 1 | 53 Before (0.02-100mL) | 5000.00000 |
| 2 | 53 After#1 (0.02-100mL) | 5000.00000 |
| 3 | 53 After#2 (0.02-100mL) | 5000.00000 |
| 4 | 53 After#3 (0.02-100mL) | 5000.00000 |

Fig. 11