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ESCA STUDIES ON LEACHED GLASS FORMS

by

B. G. Dawkins

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ESCA STUDIES ON LEACHED GLASS FORMS

B. G. Dawkins
E. I. du Pont
Savannah River Plant
Aiken, South Carolina 29801

Summary

Electron Spectroscopy for Chemical Analysis (ESCA) results for frit, obsidian, NBS standard, and Savannah River Laboratory (SRL) glass forms that have been subjected to cumulative water leachings of 36 hours show that [Na] exhibits the largest and fastest change of all the elements observed. Leaching of surface Na occurred within minutes. Surface Na depletion increased with leach time.

Continuous X-ray irradiation and argon ion milling induced Na mobility, precluding semiquantitative ESCA analysis at normal operating temperatures. However, the sample stage has been equipped with a liquid nitrogen supply and alkali mobility should be eliminated in future work.

Introduction

As part of the waste management scheme to solidify radioactive Savannah River Plant waste, the durability of the borosilicate glass matrix is being evaluated by leach tests. The leach process is apparently complex; it includes diffusion of water into the glass, breakdown of the silicate network, and formation of corrosion layers on the surface. The effects of leaching on these glass forms are vital for predicting the consequences of containment breaches during transportation and storage.

The surfaces of the glass forms (Table 1) were analyzed by ESCA before and after leaching (Figure 1). ESCA utilizes soft X-rays to eject inner shell electrons from the surface. When these vacancies are filled by outer shell electrons, "Auger (A)" electrons may be ejected. High resolution measurements of the kinetic energies of these electrons are converted to values of binding energies which are characteristic of the parent atoms and their chemical environments. With a depth of analysis of <50Å and high sensitivity (0.1 at.%), even slight changes in surface composition can be detected early in the leach process.

Experimental

The polished glass buttons were leached in 20-ml portions of static, distilled water at ambient temperature in cumulative time intervals. The samples were transferred to

the contained surface analysis facility where drying in a clean N_2 atmosphere and mounting for the ESCA vacuum bell jar were completed.

Before analysis, an Ar ion beam was used to reproducibly "brush" ∿15Å from the surface, exposing Na beneath the surface carbon layer. The X-ray source was the Kα line (1253.6 eV) from a Mg anode. Electron signals relative to Si were determined as a function of leach and analysis time.

Discussion

ESCA Na/Si signal ratios were used to follow the leach process. Na cations were the most mobile modifiers within the relatively stable SiO_2 network. The ratios can be correlated with the leaching of radionuclides from waste glass forms, selective dissolution of mobile ions, and total dissolution of the glass surface. Glass forms containing radionuclides may be run in the contained ESCA facility.

Nals/Si2p leach curves (Figure 2) show Na depletion trends in the outermost surface layer. Nals electrons represent a thin film (small escape depth) and therefore exhibit the largest and fastest change in relative intensities. Nals/Si2p ratios decrease rapidly initially, eventually leveling off after several hours of leaching. This is consistent with the buildup of a Na-depleted, SiO_2-rich corrosion layer.

Extensive Na migration (Figures 3 and 4) is observed during ESCA analysis, apparently due to local electric fields and/or local heating. Nals/Si2p ratios for SRL glasses tended to decrease with analysis time; the opposite trend was observed for the NBS standard, the obsidians, and the frit. These trends are attributable to both thermal effects and the glass composition. For example, SRL glasses and the frit contain substantially more network formers and modifiers and the "mixed-alkali effect"[1] may apply. It has been suggested that the presence of several modifiers tighten the SiO_2 network, reducing alkali migration. Increases or decreases in the Na concentration did not arise from aging in the instrument. Such changes are also apparently not the result of contamination effects from surface carbon and oxygen. In one experiment, at the onset of a stable Nals signal, Nals, Na(A), Cls, Ols, and O(A) relative intensities were essentially constant for 6 continuous hours of ESCA analysis (Table 2).

Conclusion

ESCA has been used to conveniently follow the initial leach process of various glass forms. Future efforts will include similar glasses mounted on a liquid-nitrogen cooled stage. Na migration should be substantially reduced and the

effects of leaching will be determined more quantitatively. Separation and correlation of leaching and analysis effects with composition will be continued. Then the leaching mechanism(s) in these glasses can be detailed.

[1]D. E. Day, J. Non-Crystalline Solids, 21 343 (1976).

TABLE I

COMPOSITION OF GLASS FORMS* STUDIED (WT%)

	N-7	21-13-7	21-5-7	FRIT 21
SiO_2	70.5	34.1	34.1	52.5
Na_2O	8.5	12	12	18.5
CaO	11.7	5.35	3.95	5
K_2O	7.7	-	-	-
Sb_2O_3	1.1	-	-	-
SO_3	0.2	-	-	-
R_2O_3	0.2	-	-	-
Li_2O	-	2.6	2.6	4
TiO_2	-	6.5	6.5	10
B_2O_3	-	6.5	6.5	10
Fe_2O_3	-	17.5	20.3	-
Al_2O_3	-	9.45	2.45	-
NiO	-	0.35	3.5	-
MnO	-	5.6	8.05	-

*OBSIDIANS ARE NATURAL VOLCANIC GLASSES OF UNKNOWN COMPOSITION.

TABLE II

X-RAY IRRADIATION AND CONTAMINATION EFFECTS

GLASS I-5, 14 HR. LEACH, 15Å SPUTTER

			INTENSITY VS. Si2p		
TIME (HR.)	Na1s	Na(A)	C1s	O1s	O(A)
1	1.32	.47	1.01	7.26	2.52
2	1.46	.46	1.03	7.41	2.57
3	1.47	.46	1.02	7.29	2.41
4	1.47	.49	.99	7.31	2.50
5	1.28	.48	1.03	7.06	2.43
6	1.44	.47	1.02	7.15	2.43

FIGURE 1

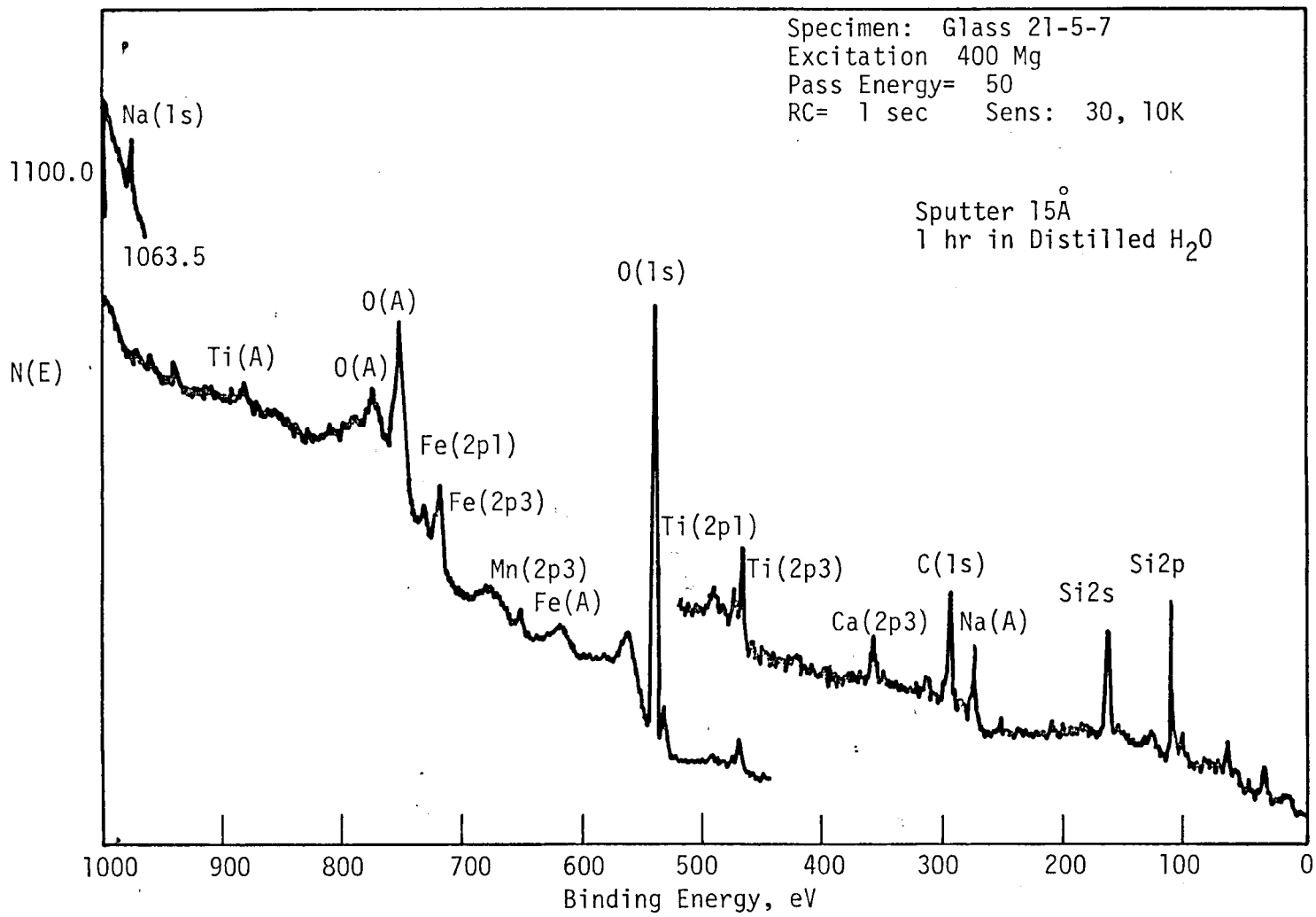

Specimen: Glass 21-5-7
Excitation 400 Mg
Pass Energy= 50
RC= 1 sec Sens: 30, 10K
Sputter 15Å
1 hr in Distilled H_2O
Na(1s)
1100.0
1063.5
N(E)
Ti(A)
O(A)
O(A)
Fe(2p1)
Fe(2p3)
Mn(2p3)
Fe(A)
O(1s)
Ti(2p1)
Ti(2p3)
Ca(2p3)
C(1s)
Na(A)
Si2s
Si2p
1000
900
800
700
600
500
400
300
200
100
0
Binding Energy, eV

FIGURE 2

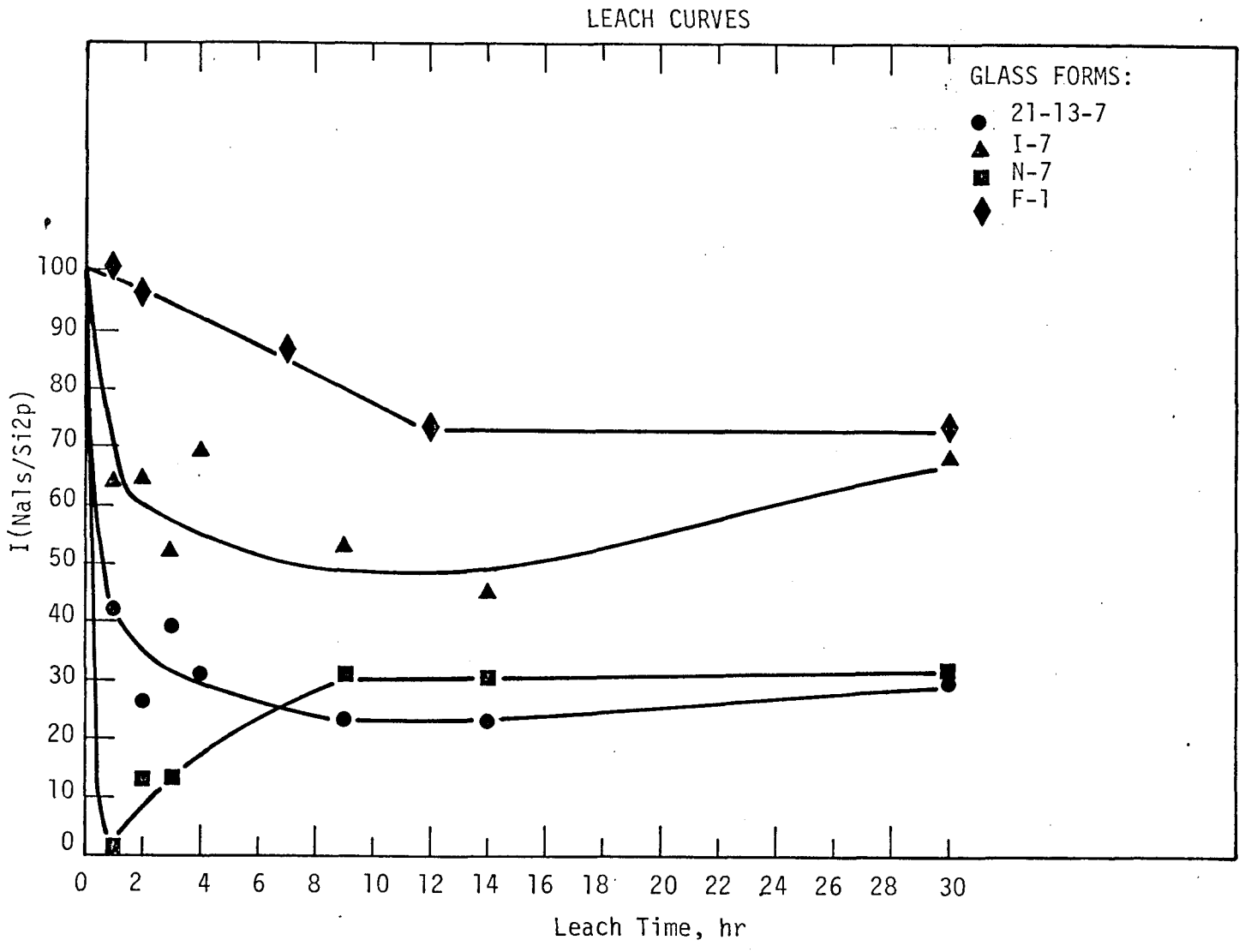

LEACH CURVES
GLASS FORMS:
21-13-7
I-7
N-7
F-1
I(Na1s/Si2p)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Leach Time, hr

FIGURE 3

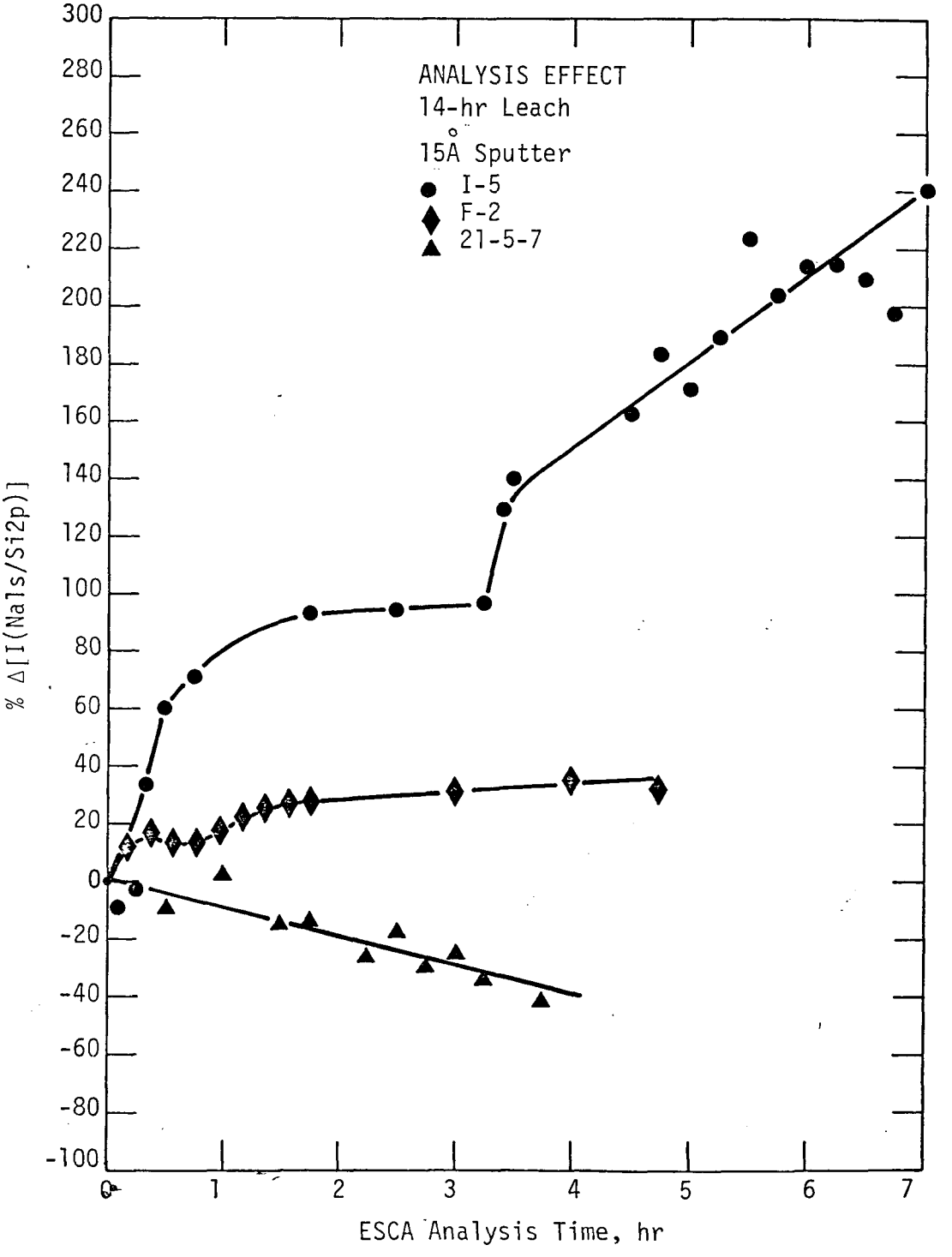
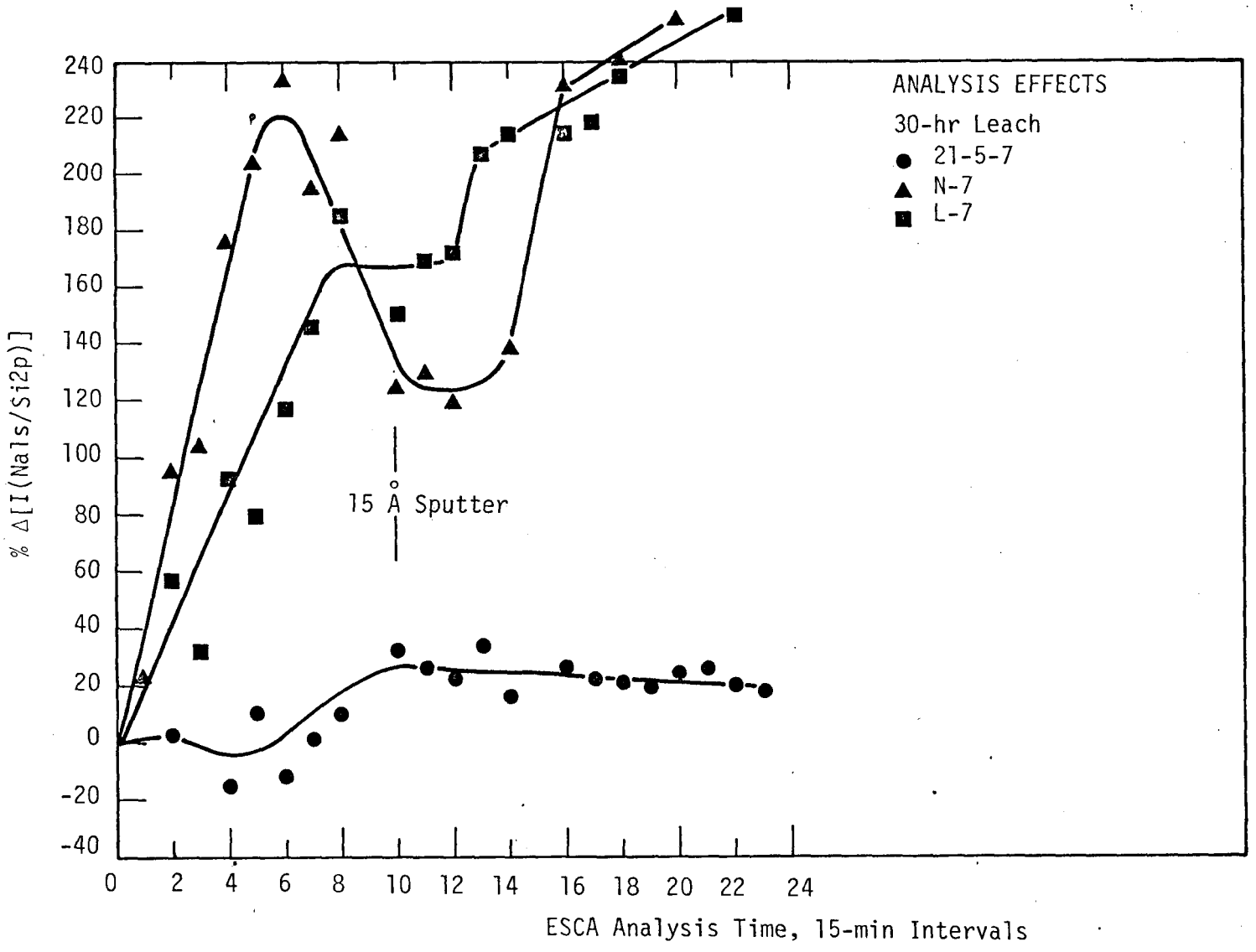

ANALYSIS EFFECT
14-hr Leach
15Å Sputter
I-5
F-2
21-5-7
% Δ[I(Na1s/Si2p)]
ESCA Analysis Time, hr
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
0
1
2
3
4
5
6
7

FIGURE 4


ANALYSIS EFFECTS
30-hr Leach
21-5-7
N-7
L-7
15 Å Sputter
% Δ[I(Nals/Si2p)]
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
0
2
4
6
8
10
12
14
16
18
20
22
24
ESCA Analysis Time, 15-min Intervals