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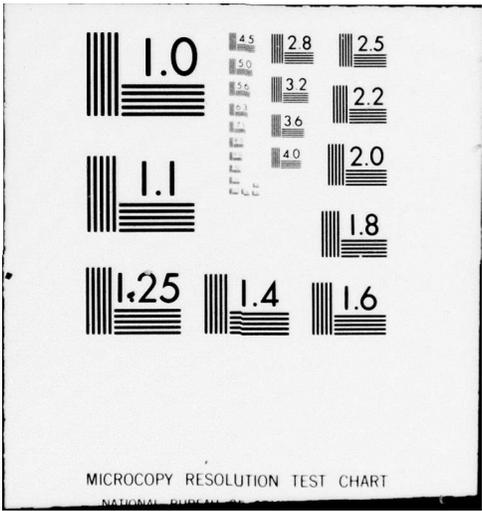
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(6) CONTAMINATION OF THE ANODE AND CATHODE IN PHOSPHORIC ACID ANODIZING ELECTROLYTES

(10) W. L. BAUN
MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

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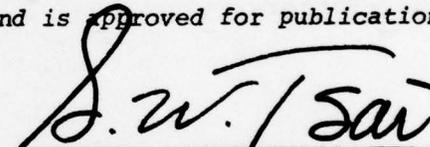
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The surface analysis of anodes and cathodes from phosphoric acid electrolytes by ion scattering spectrometry (ISS) and secondary ion spectrometry (SIMS) shows that contamination can occur under a variety of conditions. Contamination can occur both during and after anodization and either with or without the electrodes connected. These results point up the dynamic and ever changing character of the anodization process and suggests reasons for poor reproducibility of oxide chemistry and morphology.		

FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project 2419, "Nonmetallic and Composite Materials" and W.U.D. No. 44, "Improved Materials, Processes, and Life Prediction Methodology of Adhesive Bonding" monitored by T. W. Haas.

This report covers work conducted inhouse during the period July 1978-July 1979.

Helpful discussions about anodization phenomena with N. T. McDevitt are acknowledged.

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SECTION I
INTRODUCTION

The term anodization is used to denote growth of an oxide film during the application of a voltage between an anode and a cathode immersed in an electrolyte solution, which may be aqueous, nonaqueous, or a fused salt. Nine metals known as valve metals anodize readily. Several others form anodized films under very specialized conditions. Anodization of aluminum and its alloys is a well-developed technology. Diggle and co-workers¹ have reviewed anodization processes on aluminum. Aluminum anodized in sulfuric acid electrolytes forms a composite film.² A continuous nonporous layer reportedly forms next to the aluminum anode and then a noncontinuous porous layer forms between the continuous film and the electrolyte. This compounded film is excellent for many decorative and protective uses, and it is seen on automotive products, such as grills and bumpers. For capacitor dielectrics a more dense amorphous film is used and is achieved by anodization in buffered solutions of tartrates, borates, and so forth. Recently, the demand for lighter, stronger materials in the aerospace and other industries has required surface preparations for adhesive bonding of aluminum and its alloys.³ The process found most useful to date giving best bondability and long-time durability for adhesive bonding of aluminum and its alloys is the phosphoric acid anodize.^{4,5,6} It appears that the success of this anodization procedure is primarily due to the formation of a particular kind of fine porous film on the surface.⁷ The phosphoric acid anodize is accomplished in a variety of ways by various processors. Generally, however, the anodization procedure is carried out in stainless steel or lead lined tanks in approximately 0.5 to 1 molar solution phosphoric acid and at 10 to 20 volts for about 20 minutes. The character of the oxide film is determined by a balance between the rate of

formation of the oxide and the rate of dissolution. Morphology and chemistry of the oxide film are a function of the temperature, current density, and composition of the electrolyte. Surface and pore structure of a typical thick anodized oxide is seen in Figure 1. It is the purpose of this report to show the contamination that can occur both on the anode and the cathode during phosphoric acid anodization of aluminum and aluminum alloys.

SECTION II
EXPERIMENTAL

The primary characterization instrument used was ion scattering spectroscopy and secondary ion mass spectroscopy (ISS/SIMS). This dual method uses a low energy ion beam (1-3 KeV) to probe the surface. The ISS (ion scattering spectrometry) method measures the energy loss when the probing ion scatters from the outermost atom layer at the surface. The SIMS (secondary ion mass spectrometry) technique measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. Advantages and operating parameters were outlined in Part I, AFML-TR-76-29.⁸ The experimental set-up is shown in Figure 2. The two methods are very complementary, with the weakness of one usually the strength of the other. The equipment used on this work is the ISS Model 520 (3M Company, St. Paul, MN) to which was added the UTI (Uthe Technology International, Sunnyvale, CA) Model 100C quadrupole mass analyzer as shown in Figure 2. Installation of a simple three element energy filter on the front of the quadrupole mass analyzer allowed recording of +SIMS data.

Primary ion beams of $^{20}\text{Ne}^+$, $^4\text{He}^+$ and $^3\text{He}^+$ were used to scatter and sputter surface ions for analysis. Appendix A and B contain ion scattering and mass information to aid the reader in interpretation of spectra.

ISS/SIMS makes an ideal complementary tool for surface analysis. ISS is extremely sensitive to the atoms just on the surface. For aluminum oxide, ISS is very sensitive to oxide stoichiometry. However, ISS does suffer some limitations. First, the resolution of the instrument does not generally allow complete separation of adjacent elements in the periodic table.

Elements such as aluminum and magnesium are not resolved in the 90° instrument. Scattering gases may be changed to optimize resolution and/or sensitivity, but even then complete resolution may not be attained. Second, aluminum is one of the elements which exhibit severe low energy tailing, apparently due to nonbinary scattering phenomena. This effect tends to hide impurity or alloying elements. SIMS, although suffering from the limitation of widely varying ion yields, has very high sensitivity for many low z elements of interest here and provides the necessary resolution.

SECTION III
RESULTS AND DISCUSSION

The anodizing solution is an ever-changing system as will be shown by the following experiments. In the first experiment 2024 alloy of approximately one square inch was anodized in a one molar H_3PO_4 solution at 20 volts for 10 minutes, with a lead (Pb) cathode of approximately ten times the anode area. Following anodization both the cathode and anode were removed, rinsed in distilled water, and allowed to dry. ISS/SIMS data obtained at 2500 volts with 4He is represented in Figure 3. ISS spectrum 1 is that obtained during the first two-minute scan. The spectrum is similar to that frequently obtained when loose nonadhering material is present on a surface. After several minutes of sputtering, spectrum 2 was obtained which begins to show a somewhat more characteristic curve of anodized aluminum oxide. For reference the dashed curve is a typical ion scattering curve obtained under the same conditions from the natural oxide film on a polished surface. The ion scattering spectra obtained here were very similar to that recorded from PABST samples of 2024 aluminum alloy anodized in phosphoric acid by the McDonnell Douglas Company.⁹ As can be seen in ISS spectrum 1, an extremely small amount of lead is apparently present on the surface. Positive SIMS spectra shows a copper alloying element, alkali impurities, and a surprising amount of organic contamination. It is noteworthy that the secondary ion yield is considerably smaller than that normally observed from anodized surfaces. ISS/SIMS data for the matching lead cathode are seen in Figure 4. Here the normal background as seen on a clean lead specimen is shown as a dashed line. It can be seen from the ISS spectrum, that there is a considerable amount of low atomic number element contamination which appears on the cathode surface. This was a freshly prepared electrolyte; therefore, the amount of copper

shown on this particular specimen in the positive SIMS spectrum is due just to dissolution and redeposition from a single anodization. The large yield of the cluster peak AlO^+ compared to Al^+ is highly unusual and may indicate that aluminum is in a very active or hydrated state. The appearance of fluorine at atomic mass 19 in the positive SIMS spectrum is of interest. The original 2024 aluminum alloy was etched in a dilute solution of HNO_3/HF , and it appears that the fluorine which had remained on the surface has been transported through the electrolyte to the cathode surface. It is possible that the solution itself contained fluorine from the beginning but it is not likely.

The second part of this experiment, the cathode (the data for which was shown in Figure 4), was cut in half and placed back in the electrolyte with the electrodes connected but the power supply turned off. After 15 minutes it was removed, rinsed with deionized H_2O , and air dried. This experiment was expected to show the effect of one of the conditions in the electrolyte which could occur if the anodization were completed and then both the cathode and anode allowed to sit in the solution for a period before they were removed. The anode developed a smutted appearance and showed primarily copper in the ion scattering spectrum. The cathode, however, showed a large increase in the total number of impurities, as seen in the ion scattering spectrum, Figure 5. Here the count rate for lead is only about one half what it had been in the spectrum shown in Figure 4. In addition, the background of low atomic number elements is seen to be much larger than in the spectrum taken immediately after the anodization.

The same experiment as outlined above was repeated. The reproducibility of the positive SIMS and ISS data between this experiment and the earlier one was found to be excellent. It

was noticed in this experiment that the cathode which had faced away from the anode during the anodization seemed somewhat lighter in color and had less impurities on it visually. Ion scattering spectra were obtained on this cathode on both sides, the area away from the anode and facing the anode, as seen in Figure 6. Here it can be seen that the area facing the anode compared favorably with the data of Figure 3. The area away from the anode at the same counting rate as had been shown earlier for the ion scattering of the cathode. Therefore, it was found in this electrolyte and this anode/cathode combination that there was far more contamination on the cathode on the side which directly faced the anode. The second part of the experiment was then repeated with some modification. Where originally the sample had been put back into the anodizing solution and the leads connected, now both the anode and the cathode were put back into the solution, but the electrical leads were not connected. This part of the experiment was expected to determine the effect on the chemistry of the surface of disconnecting the leads following anodization, but not immediately pulling the anodized panel out of the anodizing solution. The anode, after this treatment, had now turned dull gray. The cathode was also visually contaminated. The anode, whose ISS and SIMS spectra are shown in Figure 7, now gives primarily the pattern of lead. The positive SIMS spectra also shows some of the other impurities present in the electrolyte, including copper. Positive SIMS spectra at very high atomic mass units above mass 200 showed Pb^+ and PbO^+ ions. It appears from this then that the lead has gone into solution during the period in which the anode/cathode were not connected, and then due to an electroless deposition process, the anodized workpiece became covered with lead. The cathode visually appears less contaminated than before; however, the ion scattering spectrum for lead scattering is much less intense than before, giving the appearance that the lead is

covered by some impurities. Positive SIMS spectra again only show about the same level of impurities as before, although the positive SIMS yields do vary greatly and no faith can be placed on the intensity of these ions. Perhaps rather than actual impurities being on the lead cathode surface, the lead has in some way changed chemical state. The surface has become somewhat roughened giving a poorer scattering pattern. Still another alternative is that the contamination is primarily from hydrocarbons which give a very poor ion scattering spectrum. Little quantitative conclusions can be drawn from the positive SIMS spectrum. These results indicate that the failure to remove the workpiece following the disconnect of the electrical leads produces the most contamination on the anodized surface.

Again the experiment was repeated. This time instead of using a lead cathode, a 304 stainless steel cathode was used. Anodization now produced an oxide on the 2024 aluminum which was typical of most anodized films observed earlier, showing little contamination. The stainless steel, however, showed a great deal of contamination as seen in Figure 8 not only of the elements which had been seen in previous experiments, but by lead which had gone in the solution in the work described above, where the anode and the cathode were held in the phosphoric acid electrolyte, but without the electrical leads connected. Now the amount of lead on the surface appears to have dropped as seen in Figure 9. Note that both chromium and iron are seen prominently in the positive SIMS spectrum and that the total yield of the SIMS spectrum is approximately one order of magnitude greater than in the earlier contaminated specimen. For this specimen the ion beam was switched to $^{20}\text{Ne}^+$ which provides much better dispersion for heavier elements and particularly for the chromium and iron in the stainless steel. Figure 10a shows the $^{20}\text{Ne}^+$ spectra at 2500 volts of the stainless steel

cathode on the side opposite (facing) the anode. The neon ions have a very high sensitivity for lead and show the surface to have a high coverage of lead, but some chromium and iron still are visible in the spectrum. Figure 10b shows the side which appeared much cleaner which was away from the anode in the solution, now shows no lead on that side and the signal from iron and chromium, which was essentially identical to that found from clean stainless steel.

SECTION IV
CONCLUSION

The examination of both anodes and cathodes using SIMS and ISS show that contamination of both the anode and the cathode occur under certain circumstances. Failure to remove the work-piece following anodization can create contamination in the anodized coating. Dissolution of the lead could cause problems in anodization of aluminum when using lead tanks. Whether deleterious to the coating or not, these results indicate that the anodization process is an ever changing system, and it is not surprising that problems in reproducibility have been encountered. Likewise, it is not surprising that from one laboratory to another there has been difficulty in reproducing the same chemistry and morphology of anodized films.

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APPENDIX A

ION SCATTERING DATA FOR 90° SCATTERING

(E/E_0) for $Z = 1 - 50$

ELEMENT			E/E ₀ (at $\theta = 90^\circ$)			
Z	A		³ He	⁴ He	²⁰ Ne	⁴⁰ Ar
1	1.0	H		---		
2	4.0	He	.143	0	---	---
3	6.9	Li	.393	.266	---	---
4	9.0	Be	.500	.385	---	---
5	10.8	B	.565	.459	---	---
6	12.0	C	.600	.500	---	---
7	14.0	N	.647	.555	---	---
8	16.0	O	.684	.600	---	---
9	19.0	F	.727	.652	---	---
10	20.2	Ne	.741	.669	.005	---
11	23.0	Na	.769	.704	.070	---
12	24.3	Mg	.780	.717	.097	---
13	27.0	Al	.800	.742	.149	---
14	28.1	Si	.807	.751	.168	---
15	31.0	P	.824	.771	.216	---
16	32.1	S	.829	.778	.232	---
17	35.5	Cl	.844	.797	.279	---
18	39.9	Ar	.860	.818	.332	---
19	39.1	K	.857	.814	.323	---
20	40.1	Ca	.861	.819	.334	.001
21	45.0	Sc	.875	.837	.385	.059
22	47.9	Ti	.882	.846	.411	.090
23	50.9	V	.889	.854	.436	.120
24	52.0	Cr	.891	.857	.444	.130
25	54.9	Mn	.896	.864	.466	.157
26	55.8	Fe	.898	.866	.472	.165
27	58.9	Co	.903	.873	.493	.191
28	58.7	Ni	.903	.872	.492	.189
29	63.5	Cu	.910	.881	.521	.227
30	65.4	Zn	.912	.885	.532	.241
31	69.7	Ga	.917	.891	.554	.271
32	72.6	Ge	.921	.896	.568	.290
33	74.9	As	.923	.899	.578	.304
34	79.0	Se	.926	.904	.596	.328
35	79.9	Br	.928	.905	.600	.333
36	83.8	Kr	.931	.909	.615	.354
37	85.5	Rb	.932	.911	.621	.363
38	87.6	Sr	.934	.913	.628	.373
39	88.9	Y	.935	.914	.633	.379
40	91.2	Zr	.936	.916	.640	.390
41	92.9	Nb	.937	.917	.646	.398
42	95.9	Mo	.939	.920	.655	.411
43	99	Tc	.941	.922	.664	.424
44	101.1	Ru	.942	.924	.670	.433
45	102.9	Rh	.943	.925	.675	.440
46	106.4	Pd	.945	.928	.684	.454
47	107.9	Ag	.946	.929	.687	.459
48	112.4	Cd	.948	.931	.698	.475
49	114.8	In	.949	.933	.703	.483
50	118.7	Sn	.951	.935	.712	.496

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APPENDIX B
RELATIVE ABUNDANCE OF NATURALLY OCCURRING
ISOTOPES, $Z = 1 - 44$

RELATIVE ABUNDANCES OF NATURALLY OCCURRING ISOTOPES

Z	A	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
1	H	99.9	0.1																			
2	He			100																		
3	Li				7.4	92.6																
4	Be							100														
5	B								18.3	81.7												
6	C										98.9	1.1										
7	N												99.6	0.4								
8	O														99.8	0.04	0.20					
9	F																			100		
10	Ne																					90.5
Z	A	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	
10	(Ne)	0.3	8.8																			
11	Na			100																		
12	Mg				78.6	10.1	11.3															
13	Al							100														
14	Si								92.2	4.7	3.1											
15	P										100											
16	S												95.0	0.8	4.2		0.02					
17	Cl															75.5		24.5				
18	Ar																0.34		0.06		99.6	
19	K																			93.1	0.01	
20	Ca																				97.0	
Z	A	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	
19	K	6.9																				
20	Ca		0.6	0.1	2.1		0.03		0.2													
21	Sc					100																
22	Ti					8.0	7.3	74.0	5.5	5.2												
23	V									0.3	99.7											
24	-Cr									4.3			83.8	9.6	2.3							
25	Mn															100						
26	Fe														5.8		91.7	2.2	0.3			
27	Co																			100		
28	Ni																		67.8		26.2	
Z	A	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	
28	(Ni)	1.2	3.6		1.2																	
29	Cu			69.1		30.9																
30	Zn				48.9		27.8	4.1	18.6		0.6											
31	Ga									60.5		39.5										
32	Ge										20.5		27.4	7.7	36.7		7.7					
33	As															100						
34	Se														0.9		9.0	7.6	23.5		49.8	
35	Br																			50.6		
36	Kr																		0.4		2.3	
Z	A	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	
34	(Se)		9.2																			
35	(Br)	49.4																				
36	(Kr)		11.5	11.5	56.9		17.4															
37	Rb					72.2		27.8														
38	Sr			0.6			9.9	7.0	82.5													
39	Y									100												
40	Zr										51.5	11.2	17.1		17.4		2.8					
41	Nb													100								
42	Mo												15.9		9.1	15.7	16.5	9.5	23.7		9.6	
43	Tc	DOES NOT OCCUR NATURALLY																				
44	Ru															5.6			1.9	12.7	12.6	

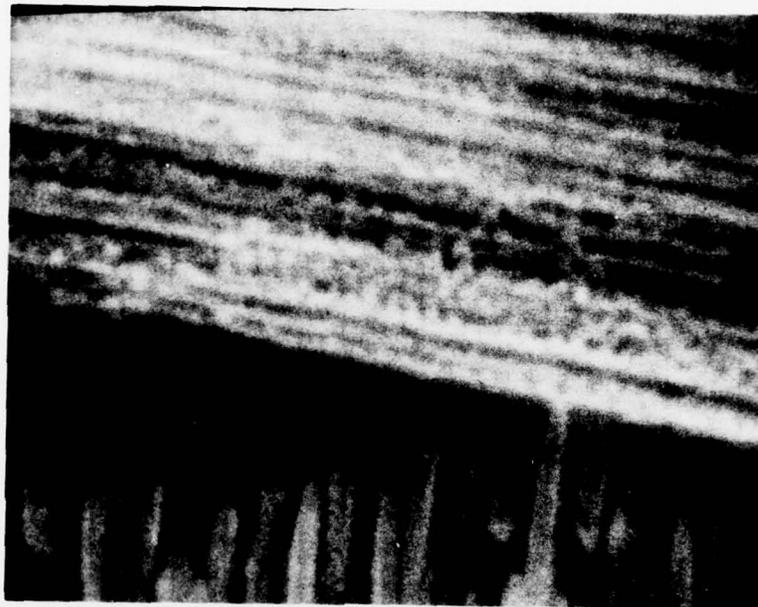


Figure 1. Scanning Electron Micrograph Showing Surface and Pore Structure of Oxide Formed on Aluminum by Anodization in 1.0M H_3PO_4 for 10 Minutes at 40 Volts.

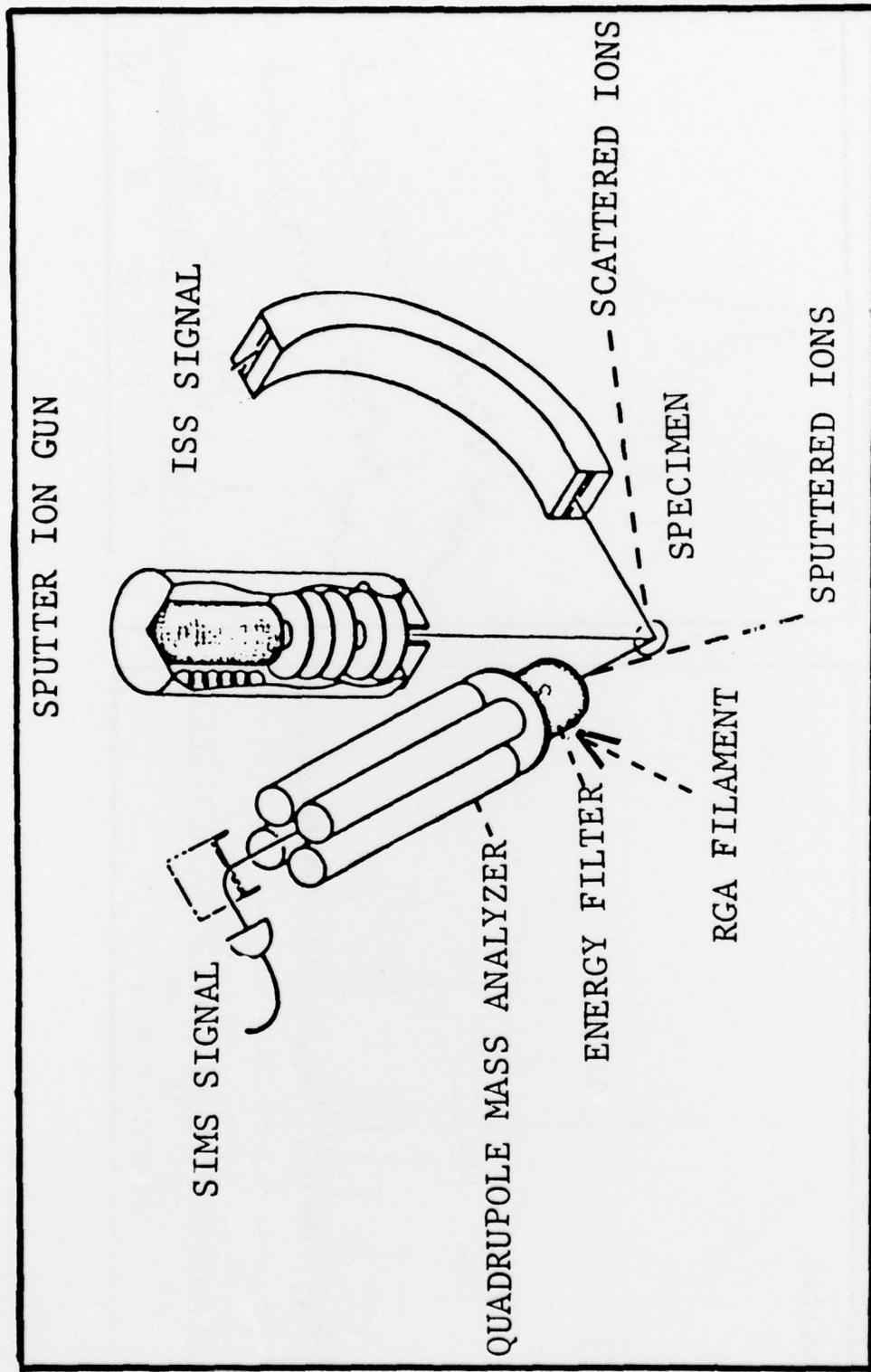


Figure 2. Components in UHV for ISS/SIMS.

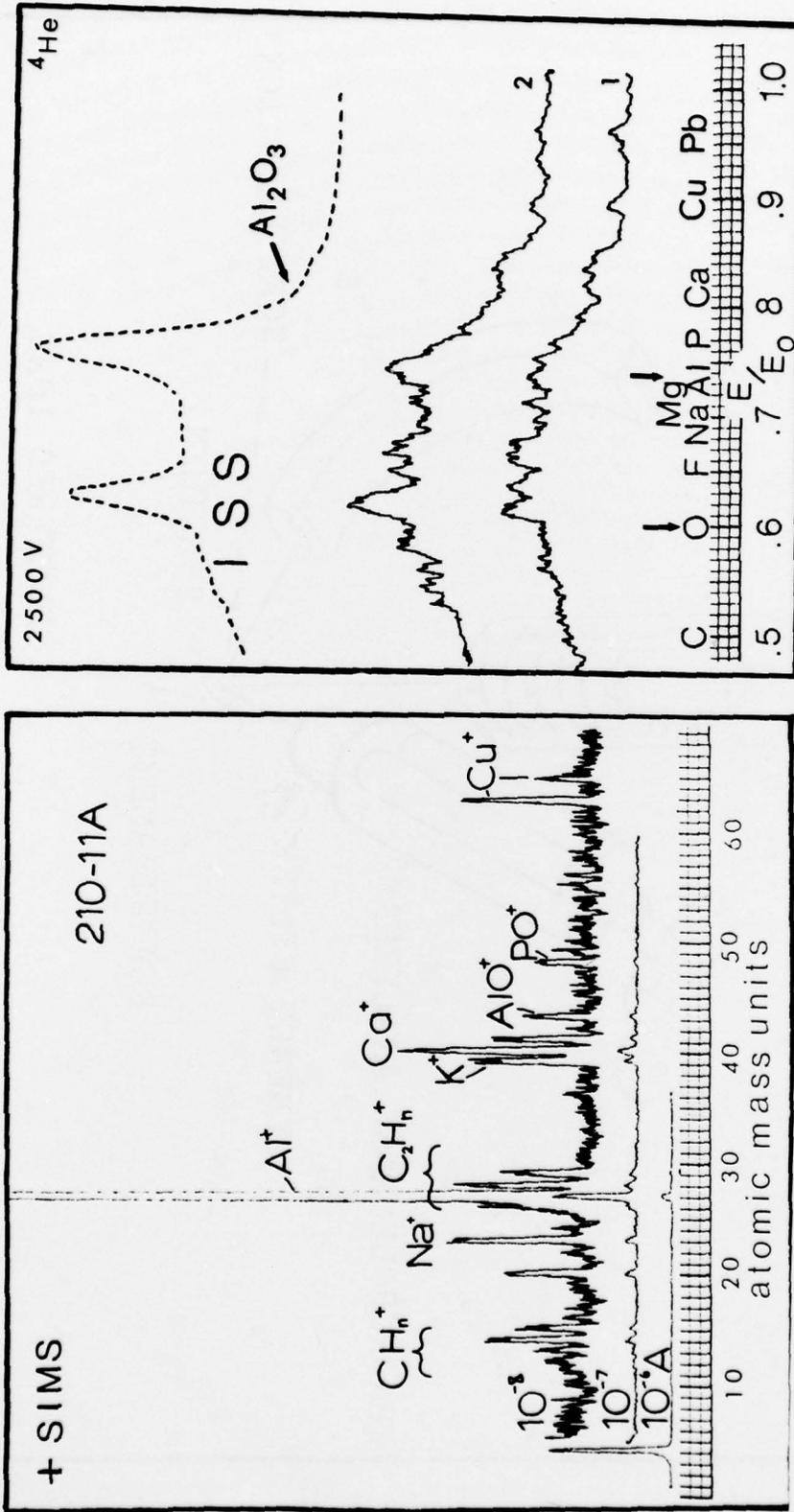


Figure 3. ISS/SIMS Data Using $^4He^+$ of 2024 Al Alloy Anodized in H_3PO_4 .

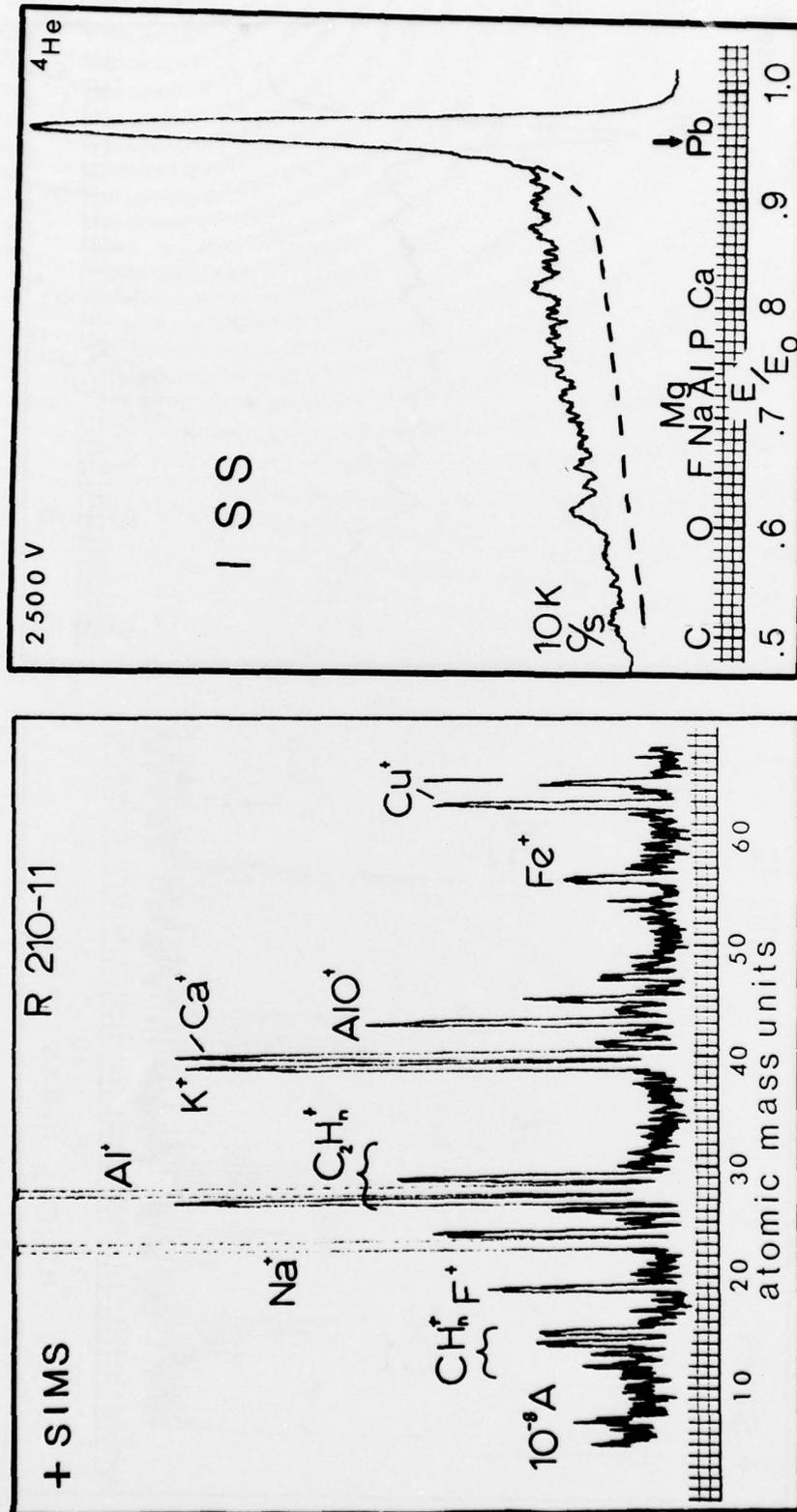


Figure 4. ISS/SIMS Data from Matching Pb Cathode from Solution Used in Sample from Figure 1.

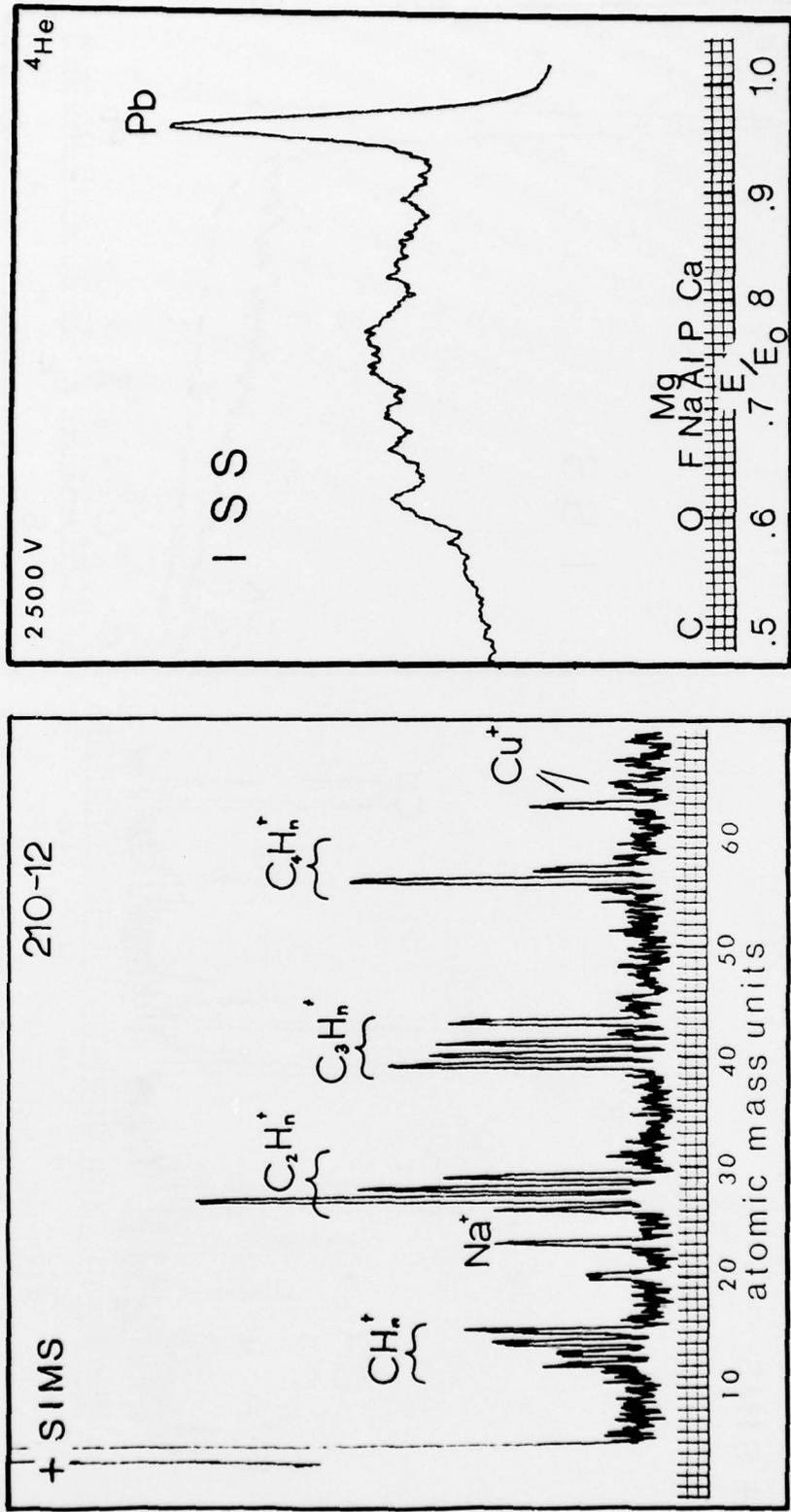


Figure 5. ISS Data from Pb Cathode After Current Turned Off with Electrical Connections Intact and Allowed to Sit in H₃PO₄ Electrolyte for 15 Minutes.

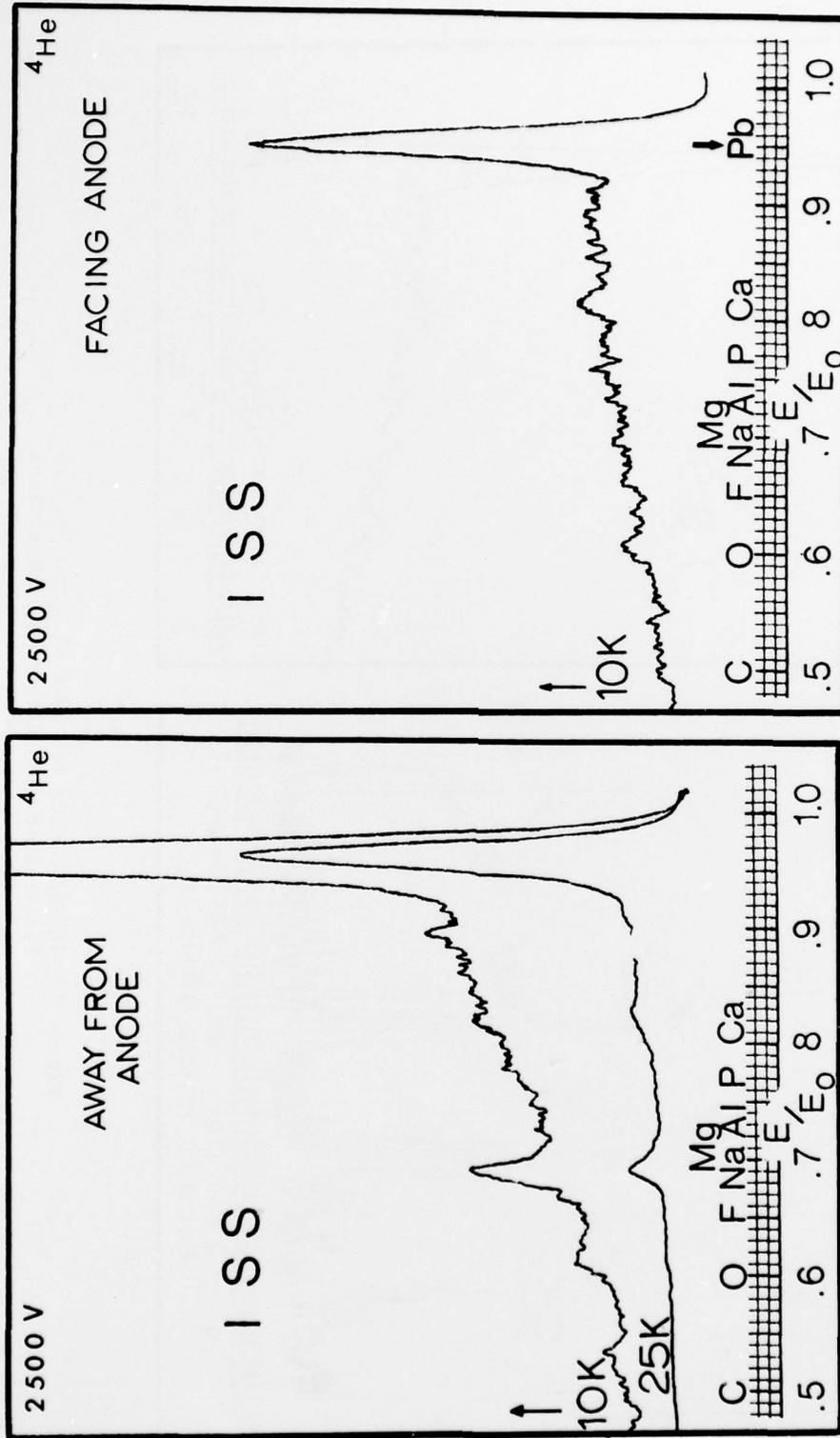


Figure 6. ISS Data for Cathode Facing the Anode and Facing Away from the Anode in an H₃PO₄ Anodizing Bath.

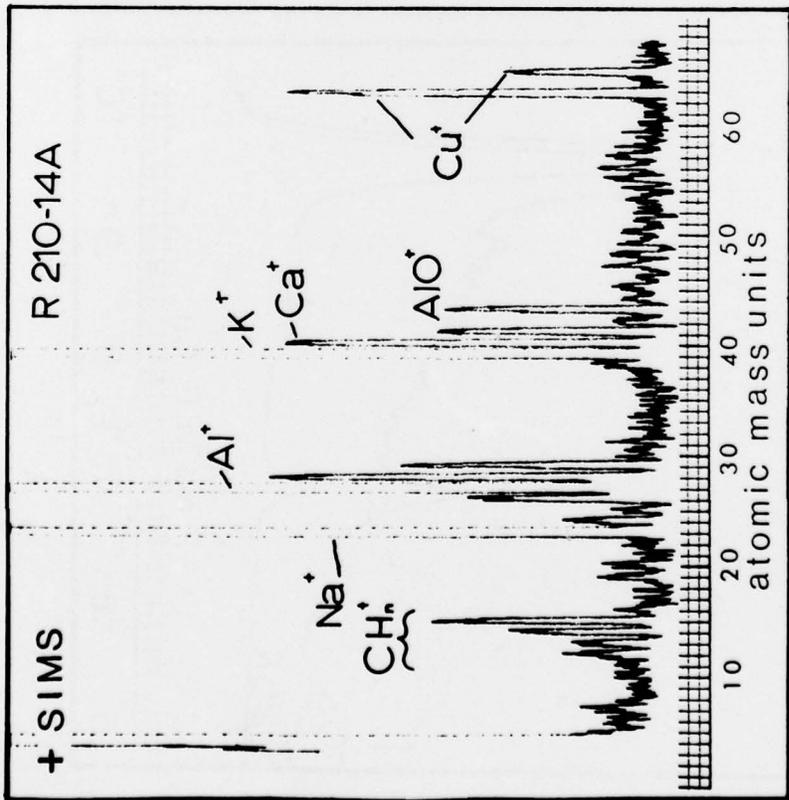
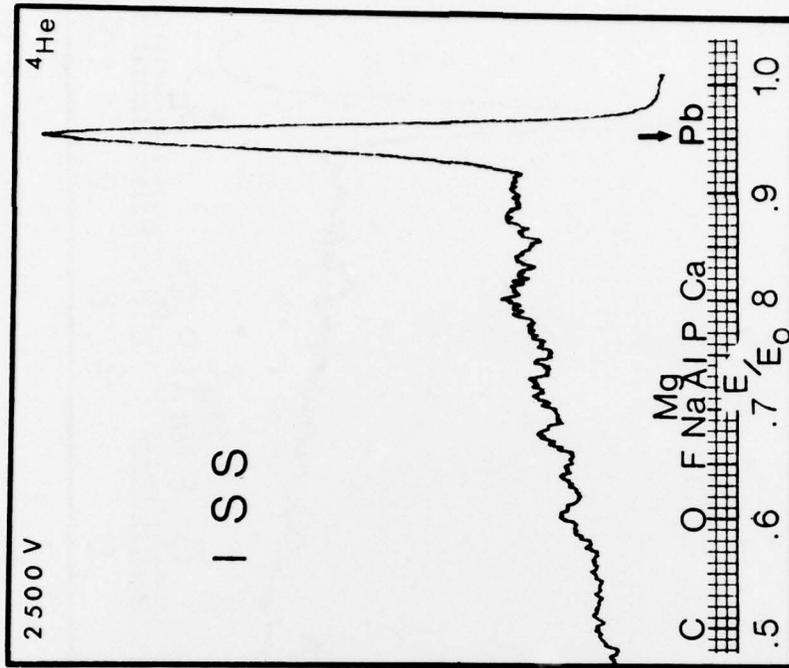


Figure 7. ISS/SIMS Data for 2024 Al Anode Held in Electrolyte with Electrical Connections Removed.

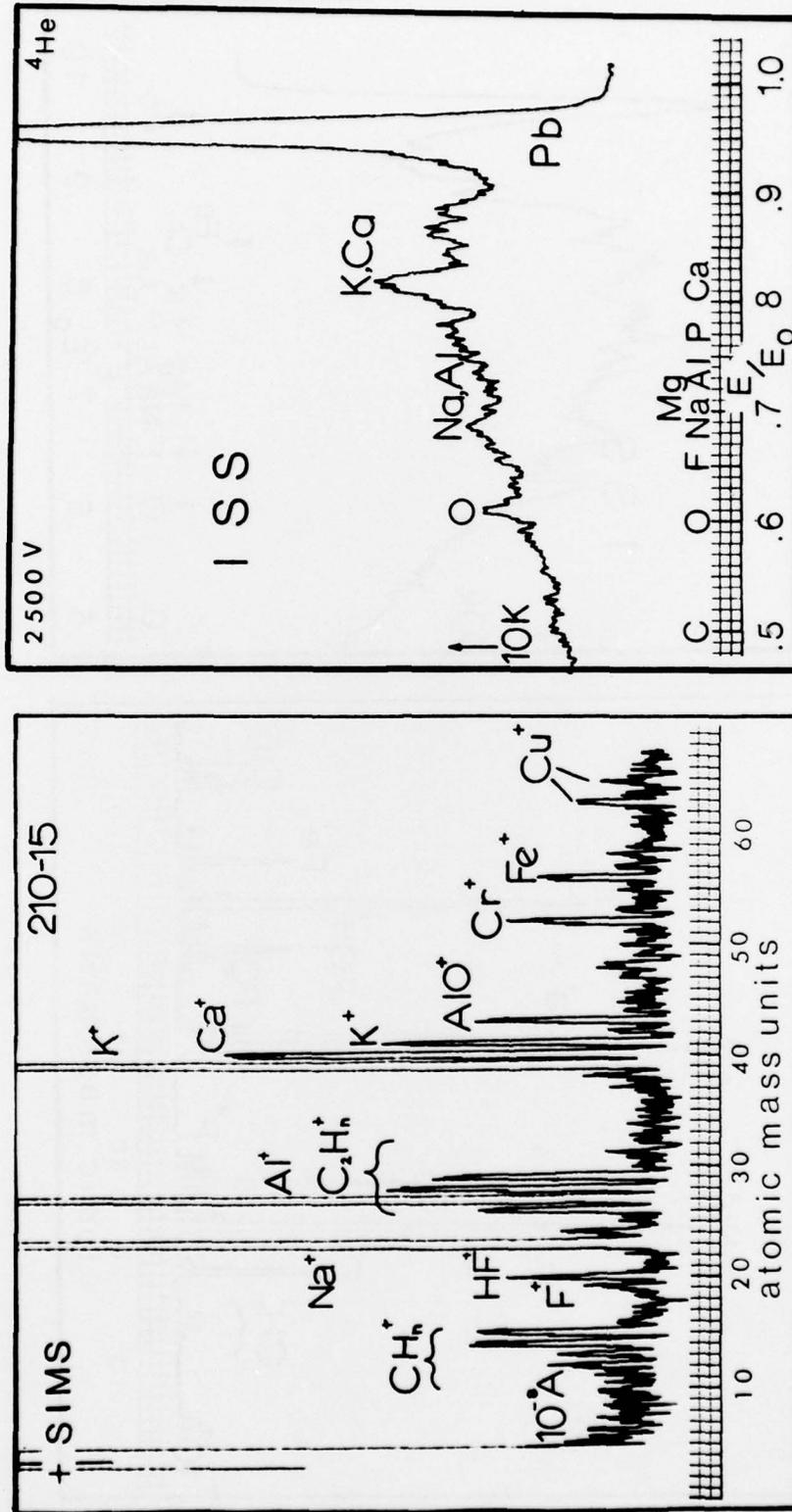


Figure 8. ISS/SIMS Data for Stainless Steel Cathode.

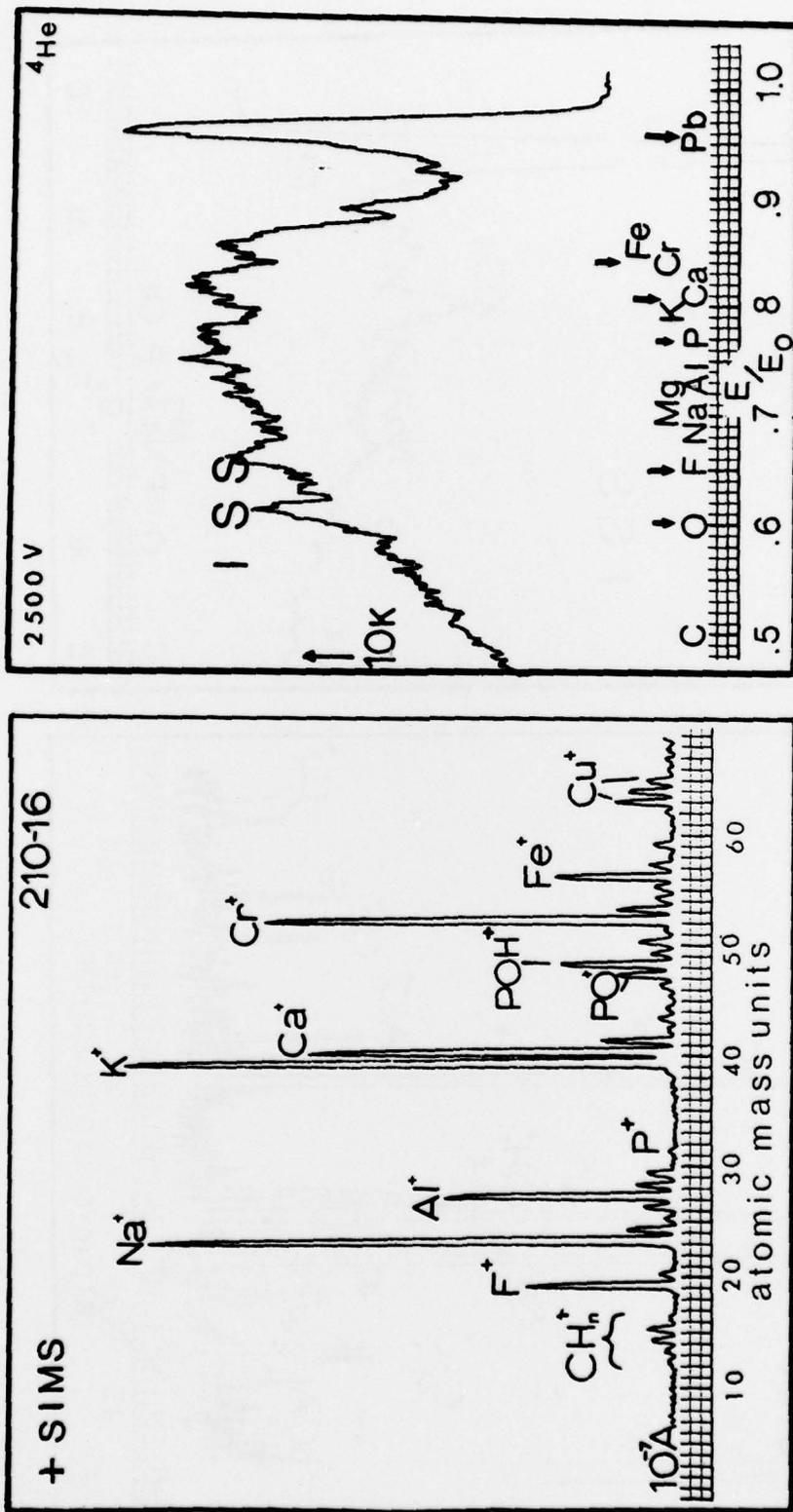


Figure 9. ISS/SIMS Data for Stainless Steel Cathode Allowed to Remain in Solution After Anodization.

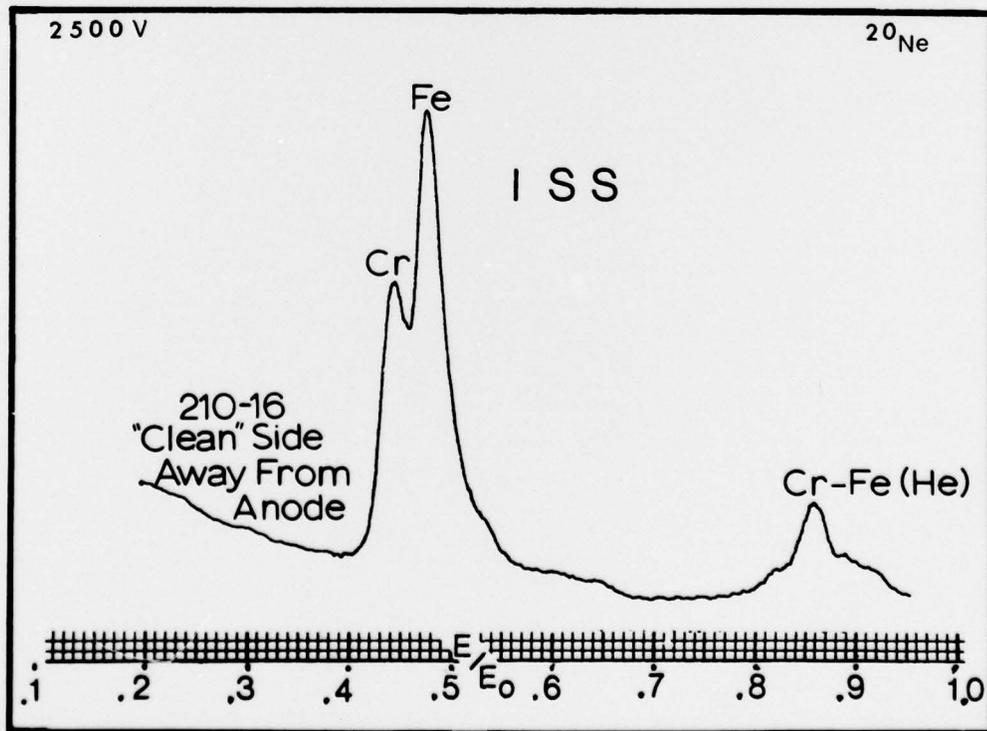
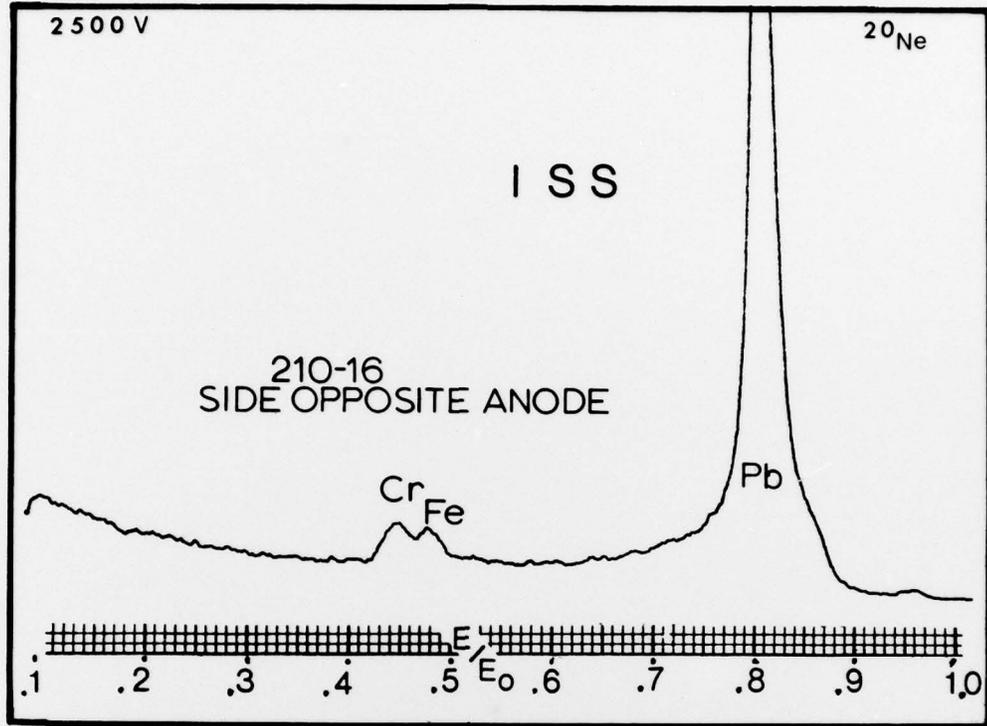


Figure 10. ISS Data for Stainless Steel Cathode:
a. Facing Anode, b. Facing Away from Anode.