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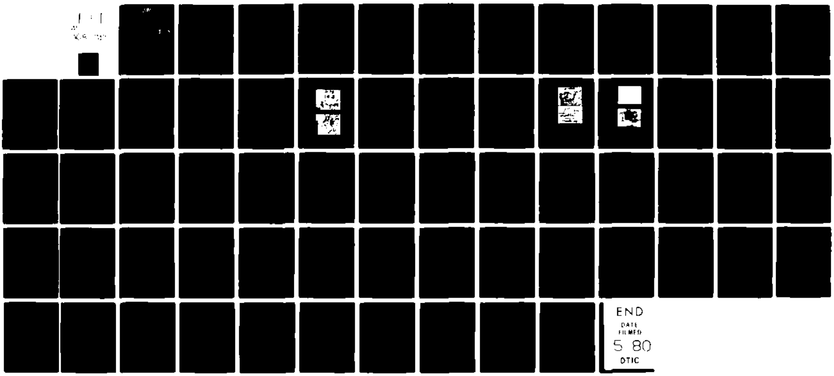

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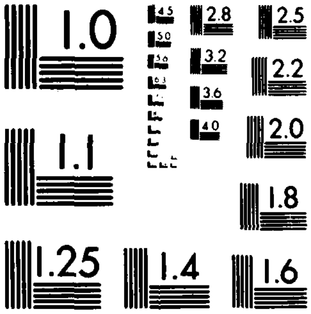

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SURFACE CHEMISTRY, MORPHOLOGY AND WETTING CHARACTERISTICS OF Ti6Al4V ADHERENDS

William L. Baun

Mechanics and Surface Interactions Branch
Nonmetallic Materials Division

January 1980

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Final Report for Period July 1978 to February 1979

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

This investigation is part of a program which looks at the effects of surface treatments on surface chemistry and morphology of titanium and titanium alloys. This part reports on the effect of surface treatments on the alloy titanium-6 aluminum-4 vanadium. Anodization as a surface preparation is considered and the effect of electrolyte pH is discussed. The chemistry, morphology, and contact angle for various treatments are described and experiments are discussed which approximate alloy use and cause changes which might be expected during the service lifetime of the alloy. No advantages are

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Contact Potential
Scanning Electron Microscopy
Adhesive Bonding
Adherend

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found for anodization and in many cases anodized films provide poorer initial bondability and long time durability than simple etched surfaces. Modification of oxides can cause large changes in contact potential, contact angle, and chemistry of oxide surfaces.

FOREWORD

This technical report was prepared by W. L. Baun, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. This work was initiated under Project 2419, "Nonmetallic and Composite Materials," and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Work unit monitor is Dr. T. W. Haas.

This report covers work conducted inhouse during the period July 1976 through February 1979.

The author wishes to acknowledge the work of James Solomon of the University of Dayton and of Gary Fugate and William Lampert. Photoelectron spectral data were obtained by M. P. Hooker (deceased), Universal Energy Systems, Inc. Timely and reliable adhesive bonding and mechanical testing were done by A. K. Behme, Jr.

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SECTION I

INTRODUCTION

The need for lighter, higher strength structures makes it necessary to develop new classes of materials such as composite and adhesively bonded materials. Unfortunately, aluminum alloys, primarily because of low melting and softening points, do not possess the properties necessary for advanced aerospace structures. Therefore, titanium and its alloys, because of lightweight, thermal stability and high strength have been under development for aerospace applications. Conventional methods of joining titanium alloys such as welding, bolting and riveting are used, but just as in aluminum alloys, the advantages of adhesive bonding make it necessary to develop surface treatments for titanium which produce adhesive joints which are strong and durable. Adhesive joints possess a more uniform stress distribution, are lighter, and are better sealed against corrosion than conventional joints. Titanium surface preparations have mostly been based on empirical use of procedures developed for other materials rather than custom processes developed strictly for the requirement with titanium.

The aerospace industry needs for operation in excess of 250°F places a severe burden on both the adhesive and the interfacial region between the adhesive and adherend in the joint. Joint failures under adverse conditions have often been blamed on the adhesive but the adherend surface may likely be the cause of failure in many cases. Surface treatments have been developed to give optimum bonding surfaces which produce durable bonded joints. This involves not only creating a surface of the proper structure and roughness, but also of the correct chemistry to ensure long time use under adverse conditions. It is therefore necessary to be able to determine elemental composition and morphology for a surface following each surface treatment. Certain treatments may be used to strip off the natural oxide in preparation for a treatment such as anodization, where the natural oxide is replaced by the anodic oxide of carefully controlled thickness. Other treatments etch the surface to provide mechanical (hook and latch) attachment of adhesive to adherend. Still others replace the natural oxide with a chemically formed oxide or conversion coating which is both bondable and durable. Each of these types of treatments along with their advantages and disadvantages have been described in the literature (References 1-16).

In this work, we are investigating the effects of various surface treatments on the surface chemistry, morphology and wetting characteristics of titanium and its alloys. Earlier results were reported for commercial treatments on Ti6Al4V (Reference 1), laboratory treatments on the same alloy (Reference 2), and laboratory treatments on pure titanium and Ti-8Mn (Reference 3). In this present work we discuss anodization and other surface preparations for Ti6Al4V in relation to the strength and durability of adhesive bonds prepared from these adherends.

SECTION II

EXPERIMENTAL

1. EQUIPMENT

a. ISS/SIMS

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 (3M Company, St. Paul, Minnesota) 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 Reference 1 and the experimental setup was shown in earlier reports (References 1,2). Appendices of mass and scattering information appear in this report and were also included in References 1 and 2 to aid the reader in spectral interpretation.

b. AES

Auger electron spectroscopy (AES) is based on the process of radiationless de-excitation of an excited atom by emission of electrons. This mechanism is often more probable than the radiative de-excitation by emission of an x-ray. For the matrix and alloying elements of concern in this work, the Auger electron yield per K electron vacancy is much higher than for the other mechanism of de-excitation, x-ray emission. The instrument used and described in Reference 2 is the Model 540 thin film analyzer (Physical Electronics, Inc., Eden Prairie, Minnesota), to which was added a Model 1100 quadrupule mass analyzer to allow residual gas analysis and SIMS measurements. A three element energy analyzer was installed on the quadrupule mass analyzer to allow SIMS measurements simultaneously with AES measurements.

AES has the considerable advantage that elemental profiles with depth can be relatively easily obtained. This is accomplished by slowly eroding away the surface of a fairly large area with an inert gas beam in much the same way the surface is probed for ISS/SIMS. In this AES technique, however, a much smaller beam of electrons impinges on the sample in the center of the larger ion beam. Then Auger electron peak to peak intensities are automatically plotted vs. sputtering time. Oxide thicknesses can be calculated from such data and an idea of interfacial sharpness may be gained. ISS/SIMS may also be used to measure changes with depth, but unless rastering and gating of the beam are used, cratering effects smear out the interface and make results difficult to interpret.

c. PES

Photoelectron spectroscopy (PES) sometimes called ESCA, Electron Spectroscopy for Chemical Analysis, analyzes the electrons emitted from a substance upon irradiation with x-rays. PES reproduces directly the electronic level structure and provides a powerful method to investigate chemical bonding in molecules. The equipment used here is supplied by Physical Electronics, Inc.

d. SEM

The scanning electron microscope (SEM) used in this work was the Quikscan (Coates and Welter Corporation, Sunnyvale, California).

e. Contact Potential

The contact potential measurements were made on uncharged specimens using the Model 144 Isoprobe Electrostatic Voltmeter (Monroe Electronics, Inc., Middleport, N. Y.) with vacuum evaporated gold as the reference.

SECTION III

RESULTS AND DISCUSSION

1. PREPARATION METHODS

The chemistry of Ti6Al4V surfaces after selected commercial treatments has been mentioned by several investigators (References 1,4,5,6,7,8) and SEM photographs for commercial treatments have been shown in numerous reports (References 1,4,5,6,7,9,10,11,12,13,14,16). Effects of anodization with respect to adhesive bonding were shown by Lively (Reference 12) and others (References 15,16).

Preparation of titanium alloy surfaces is aimed at the development of a strong adherent surface oxide or conversion film. Although natural oxides generally result in strong adhesive bonds, long time durability of these films is not adequate. In aluminum and some other adhesively bonded materials, in addition to producing a surface that is bondable and durable, one must also be concerned with imparting some degree of corrosion resistance to the surface. Such a requirement is not the case for titanium where a very high degree of inherent corrosion resistance is present. The numerous preparation methods for titanium usually fall into the categories of cleaning, etching, converting of the surface to a desired oxide or conversion film, and finally the modification of this film for good bonding. Examples of some possible methods for each of these steps is shown in Table 1. Several of these steps may be combined as suggested in the table or in many cases one or more of the steps may be omitted. Most surface preparations stop after the conversion step but the modification of the oxide or conversion film may prove of use. Certainly this modification step does modify the physical properties of oxide film as will be shown later.

TABLE 1

SURFACE PREPARATIONS OF TITANIUM ALLOYS FOR ADHESIVE BONDING

1 Clean	2 Etch	3 Convert	4 Modify
Solvent	Acids	Chemical	Boiling H_2O
1. Liquid	HF, HNO_3,	Phosphates,	Boiling H_2O + ?
2. Vapor	H_2SO_4,	Fluorides,	Dry Heat
Abrasion	H_3PO_4	etc.	Heat + Humidity
Alkaline	Combinations	Anodization	Absorption
Combinations	Alkaline	dense	UV, ions,
	Abrasive	porous	Corona, etc.
	Slurry	Combinations	

Titanium surfaces are routinely cleaned with solvents by immersion, spray or wipe. Ultrasonic cleaning with a suitable solvent and a liquid rinse is often used for small parts. There are certain conditions such as chlorinated solvents for vapor degreasing which should be avoided since they have been shown to cause stress corrosion cracking in titanium alloys. However, probably as long as this treatment is used in an early step followed by acid pickling no problem would be encountered with stress corrosion cracking. Abrasive treatments such as grit blasting, sanding, and rubbing with an abrasive pad all prove useful for cleaning highly soiled items. Alkaline treatments are frequently used in a concentration which removes contamination but does not etch the surface. Sometimes the same formulation is used in greater concentration to achieve both cleaning and surface etching. Alkaline cleaning and etching as a virtual one part preparation method appear attractive not only for their relatively low cost and safety compared to the multiple techniques using acids but also the oxides that are formed by these methods appear to be highly bondable (References 13,14).

Most surface preparation methods for titanium have as their base an acid etch which may use one acid or a combination of acids to achieve a relatively rough surface which provides a wettable surface and imparts strength to the adhesive bond by the hook and latch method. Nitric/hydrofluoric acid mixtures are frequently used for pickling or removal of oxides and etching. The hydrofluoric acid in the solution does the dissolution and removing of some of the metal while the nitric acid simultaneously oxidizes and provides a passivation layer. The primary concern in the use of acids in titanium processing is hydrogen embrittlement. The formation of hydrogen is inherent in acid etching and also in anodizing and the pickup of hydrogen on the titanium surfaces can result in embrittlement. Mechanical properties of the titanium adherends were tested after treatment in the same solutions used for the surface preparation and found to cause no hydrogen embrittlement. Only when surfaces were etched for long periods of time in very concentrated solutions was any loss of strength noted and then probably primarily due to a loss of material from the sample (i.e., the sample thickness was reduced). Sometimes, the use of acids is combined with abrasion in treatments such as the Vought Abrasive Slurry Treatment (VAST) (Reference 15). This treatment is shown in Table 2 as an example of a complete combination process for forming a stable surface for adhesive bonding. The VAST treatment leaves the surface in a highly active and very rough surface as seen in Figure 1. Concentrated alkaline etches also produce rough surfaces which are extremely bondable and as mentioned earlier these processes have the advantages of somewhat safer operation than acid techniques. Simple solutions using various concentrations of sodium hydroxide may be used, but more often proprietary mixtures such as Turco 5578 are used (Turco Products Division of Purex Corporation).

Sometimes the conversion step is included with the etching where passivation occurs following the initial etching. This usually results in a very thin oxide film. Chemical conversion in a solution containing other ions is typified by the phosphate fluoride commercial treatment. In this process the hydrofluoric-nitric acid pickle is followed by immersion in a hydrofluoric acid-phosphate-fluoride solution (References 5,7). Phosphate-fluoride treatment produces a uniform film of an average thickness of about 200°A (Reference 7). Oxide films of virtually any thickness may be obtained with high reproducibility on titanium and its alloys using anodization. Anodizing has not been commonly used as a surface treatment for titanium mostly because the possibility of hydrogen pickup and embrittlement as discussed earlier. However, in this work using both tensile and notch tests, no affect was observed. Perhaps embrittlement is encountered when using higher concentrations in solutions used for decorative anodizing. In some of these solutions which use up to 15% by weight sulfuric acid plus at times other additives there is a much greater possibility for hydrogen pickup. Titanium and

TABLE 2

THE VOUGHT ABRASIVE SLURRY TREATMENT FOR TITANIUM ALLOYS (Reference 5)

VAST with H_2SiF_6 (Reference 5)

1. Wipe surface with methyl ethyl ketone
2. Alkaline Clean - Turco 5578, 5 oz/gal
3. Rinse with D.I. water at room temperature
4. VAST process 2% H_2SiF_6 5-10 minutes
5. Rinse tap water spray at room temperature
6. Immerse one minute in solution 5% HNO_3 (optional depending on titanium alloy)
7. Rinse D.I. water at room temperature
8. Air Dry

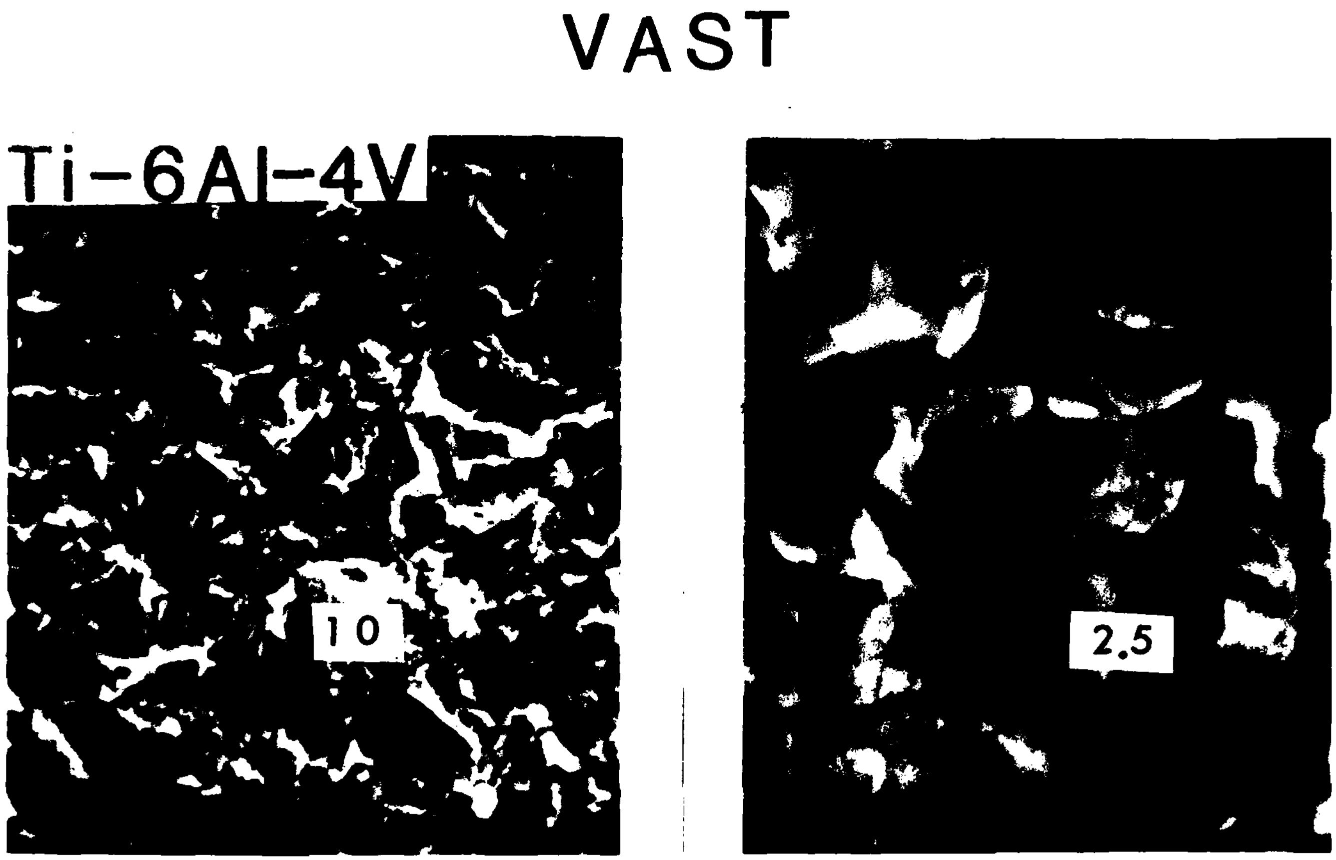

Figure 1. Scanning Electron Micrographs of Vought Abrasive Slurry Treatment on Ti6Al4V

its alloys may be anodized in a variety of solutions as shown by the review of Aladjem (Reference 17). Although these anodized films appeared to show good initial bondability using simple tests such as the lap shear, other simple tests and tests of long time durability show that anodization offers no benefit. Perhaps on the other hand anodization of titanium and its alloys will prove similar to that of aluminum alloys where it was only necessary to find the right electrolyte and the anodizing conditions to form a bondable, durable surface (References 18,19).

The modification of the "final film" is not in extensive use although the oxide is inadvertently modified in many processes by steps such as long time rinsing in hot water. The final solutions that the adherend "sees" in the processing has a very large affect on the chemistry of the film and at times on the thickness and morphology. For instance if tap water is used to rinse a specimen in which fluorine has been left behind on the surface, the surface of the titanium acts as a scavenger for ions such as calcium in the tap water. A modification step could be purposefully designed to enhance the surface for adhesive bonding using the techniques shown in Table 1 or some other method.

2. ANODIZATION OF Ti6Al4V

Table 3 shows the anodization conditions for samples 197-1 through 5. Here the affects of pH and voltage were investigated using four different solutions. When anodization was carried out in each of these solutions at low voltages and the voltage was increased by steps there was first a large increase in the current in the system followed by a rapid decline to near zero. At each of these voltage steps titanium alloys changed colors. These colors are extremely vivid, ranging from deep blues to brilliant golds. Colored films become visible at only a few volts and are very intense in the region of 10 to 100 volts. Assuming approximately 15 to 20 Angstroms per volt in most electrolytes.

TABLE 3

ANODIZATION CONDITIONS

All samples cleaned prior to anodization with abrasive pad and detergent.

Sample		Electrolyte
Neutral	197-1	$Na_2HPO_4 + H_3PO_4$ (pH 7)
	A	50V (yellow)
	B	20V (blue)
	C	100V (grey) with sparking
	197-2	Same as 197-1 but abrasive pad not used
Base	197-3	0.1M NaOH (pH 12.4)
	A	50V (yellow)
	B	20V (blue)
	C	200V (grey) with current instability and hissing
Acid	197-4	0.1M H_3PO_4 (pH 1.80)
	A	50V (yellow)
	B	20V (blue)
	C	250V (grey) with hissing at meniscus and current instability
Acid	197-5	0.1M H_2SO_4
	A	50V (yellow)
	B	20V (blue)
	C	100V (grey) hissing with slight visible light emission

This range of thicknesses would then be 150 to 2,000 Angstroms. Titanium and the other valve metals when they form anodic oxides exhibit interference colors which result in colored oxide films. Light incident on the air/oxide interface is partially reflected and partially transmitted. A portion of the light that is transmitted through the oxide strikes the oxide metal interface, is partially reflected, and partially absorbed. The total light reflected from the oxide metal combination may be considered as the sum of two contributions. The first of these is the light which is reflected at the air/oxide interface and never passes through the oxide and the second contribution consists of light which is passed through the oxide two or more times before being emitted at the air/oxide interface. These two portions of light are in phase only in specific wavelengths because of path length differences and phase changes occurring on reflection. The intensity of light reflected is then a function of the wavelength of the incident light, the thickness of the oxide film, and the optical properties of both the oxide and the metal. When these oxides are removed such as in the work in this laboratory on strippable films, the colors are much different from the vivid colors exhibited while on the substrate and are much less intense. For instance, anodized films exhibiting bright reflections actually were pale yellow in transmission. It is the color in reflection which is noted in Table 3 for samples A and B. Sample C is a porous film and is produced using a voltage at which when the voltage is increased the current no longer drops to near zero and at times sparking or hissing is observed. The surface morphology of the thin oxide films do not generally appreciably modify the original appearance of the surface. An example of this for two electrolytes is shown in Figure 2. Here Ti6Al4V was anodized in phosphoric acid at 20 volts shown in A and in phthalic acid also at 20 volts as shown in B. The anodized surfaces shown appear to be relatively smooth with the original surface scratches very distinct. However, when the anodization voltage is increased to 300 volts as seen in Figure 3 the porosity is quite clearly seen. These two electrolytes as well as each electrolyte that was investigated in this work produced surfaces having a different

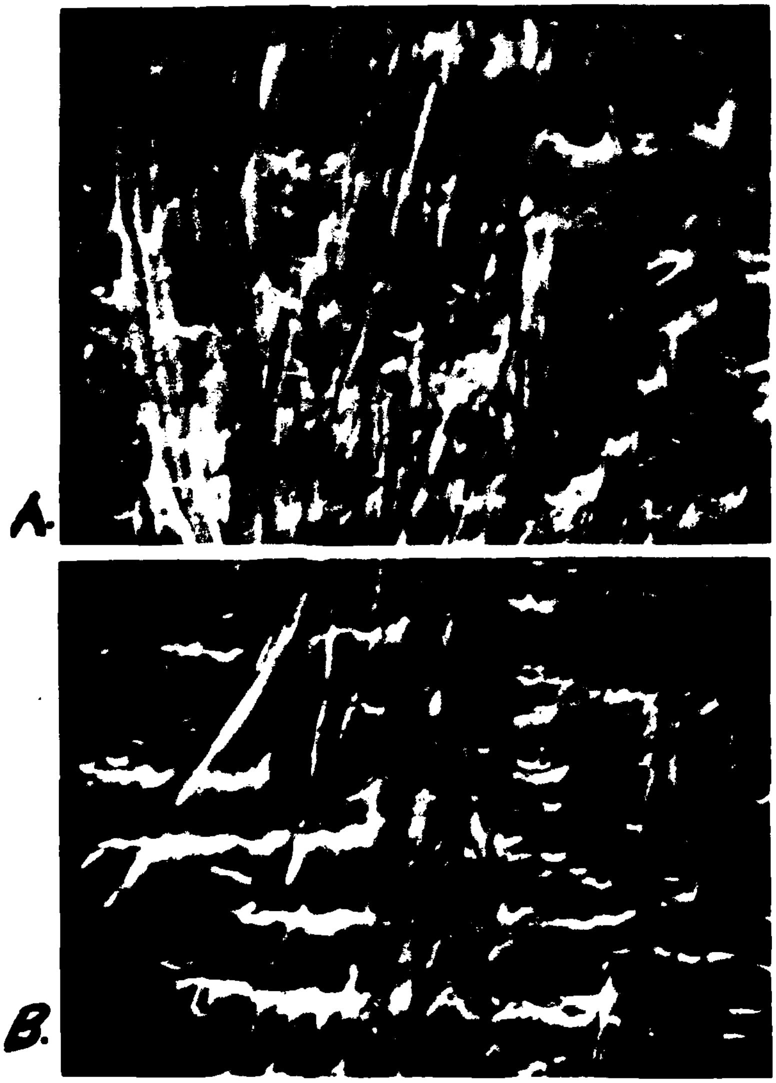

Figure 2. Thin Oxide Formed at 10 Volts Using Phosphoric Acid (a) and Phthalic Acid (b)

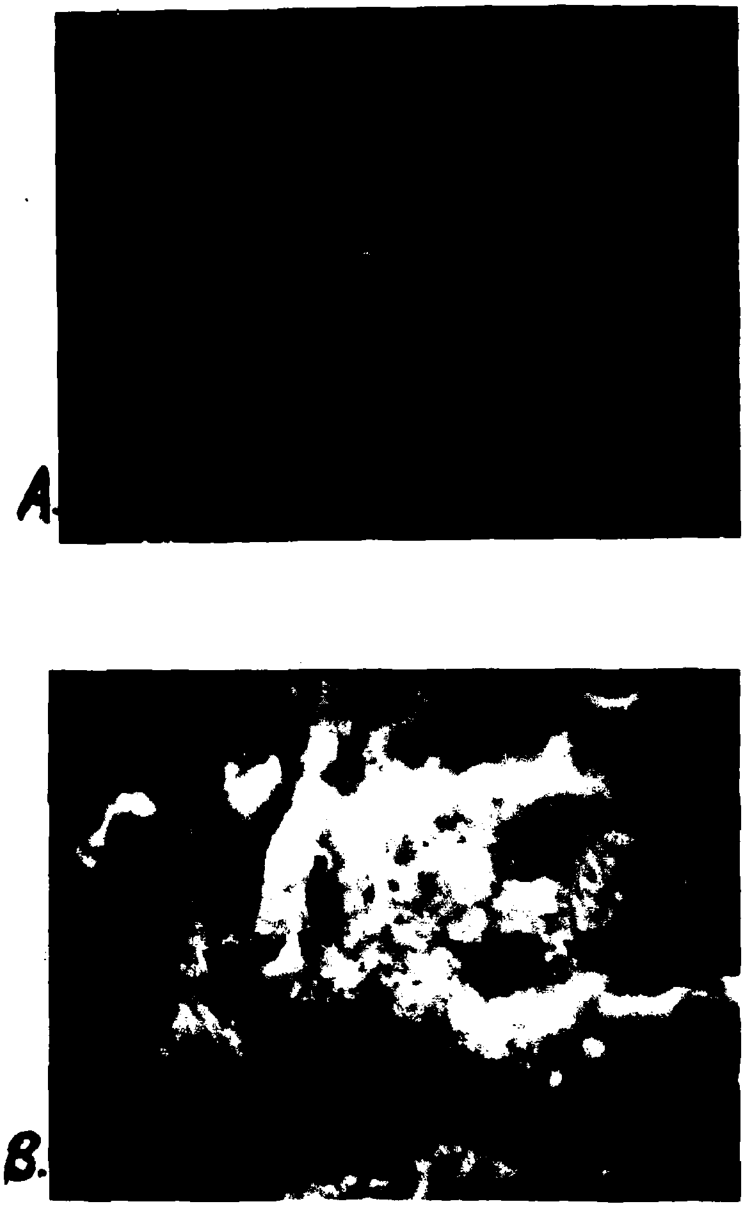

Figure 3. Thick Porous Oxide Produced at 300 Volts in Phosphoric Acid (a) and in Phthalic Acid (b)

morphology and some amount of porosity at higher voltages (beyond the point at which the interference colors are observed). The surface chemistry of the thin oxides typified by Figure 4 (Sample 197-1A) is similar to that observed for TiO_2 with the oxygen to titanium ratio in the ion scattering spectrum giving approximately the same value as that obtained from pure rutile. Alloying elements and impurity ions are also observed as in the SIMS spectrum. The surface chemistry of the porous anodized oxides however, are significantly different as seen in Figure 5 which is typical of oxides formed particularly in media containing phosphates and shows much different ISS and SIMS data as compared to the dense oxide. The SIMS spectrum shows hydrocarbons, alkali elements, calcium, and most importantly evidence of phosphorous or phosphate ion in the oxide film. The ion scattering spectrum also shows a large amount of phosphorous in the oxide. This appears to be bulk phosphorous in the oxide since it does not change as sputtering proceeds into the surface of the oxide. Photoelectron spectra as seen in Figure 6 also show appreciable amounts of phosphorous to be present. Also there is a much larger oxygen-titanium ratio observed in the porous oxide compared to the dense oxide. This probably suggests that much of the surface and the oxygen is combined as phosphate. The surface chemistry of other dense oxides regardless of the electrolyte that was used for anodization is essentially the same as most titanium oxides as typified by the SIMS and ISS data of Figure 7. Note in the ISS and SIMS data for the porous oxide formed in sodium hydroxide in Figure 8 that the oxide although grey in color and having exhibiting instability and hissing has not achieved the degree of porosity as seen in the oxide formed in the neutral solution. Note that in all the typical anodized oxides the TiO+ to Ti+ ratio is very high. The meaning for this phenomenon is not known but this may provide a very important clue as to the surface receptivity for adhesive bonding. In acid media again containing phosphate the porous oxide is atypical for standard titanium oxide as seen in Figure 9 where large amounts of impurities are again present with little appearance of Ti+ and TiO+. The Auger

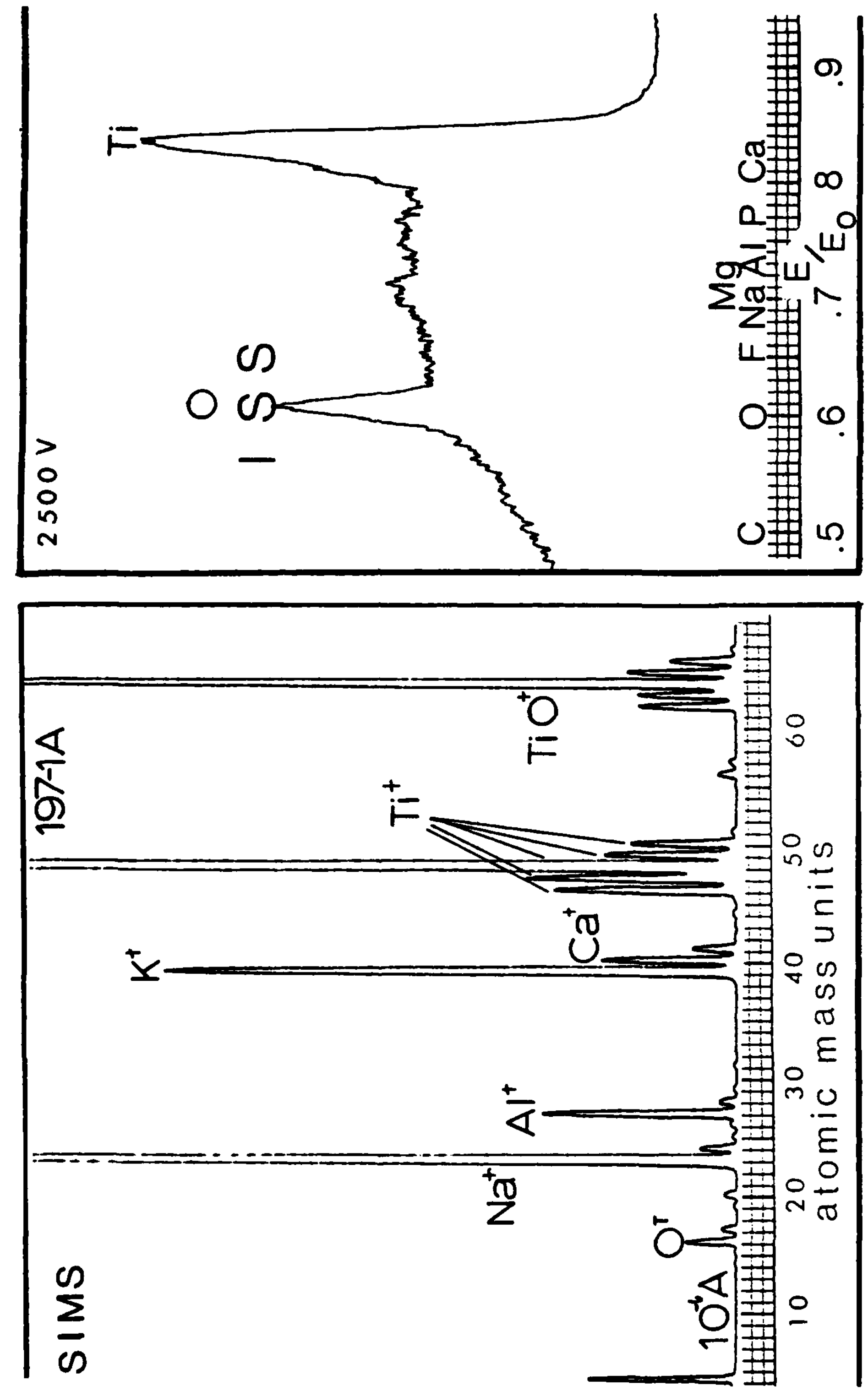

Figure 4. ISS/SIMS Data for Sample 197-1a

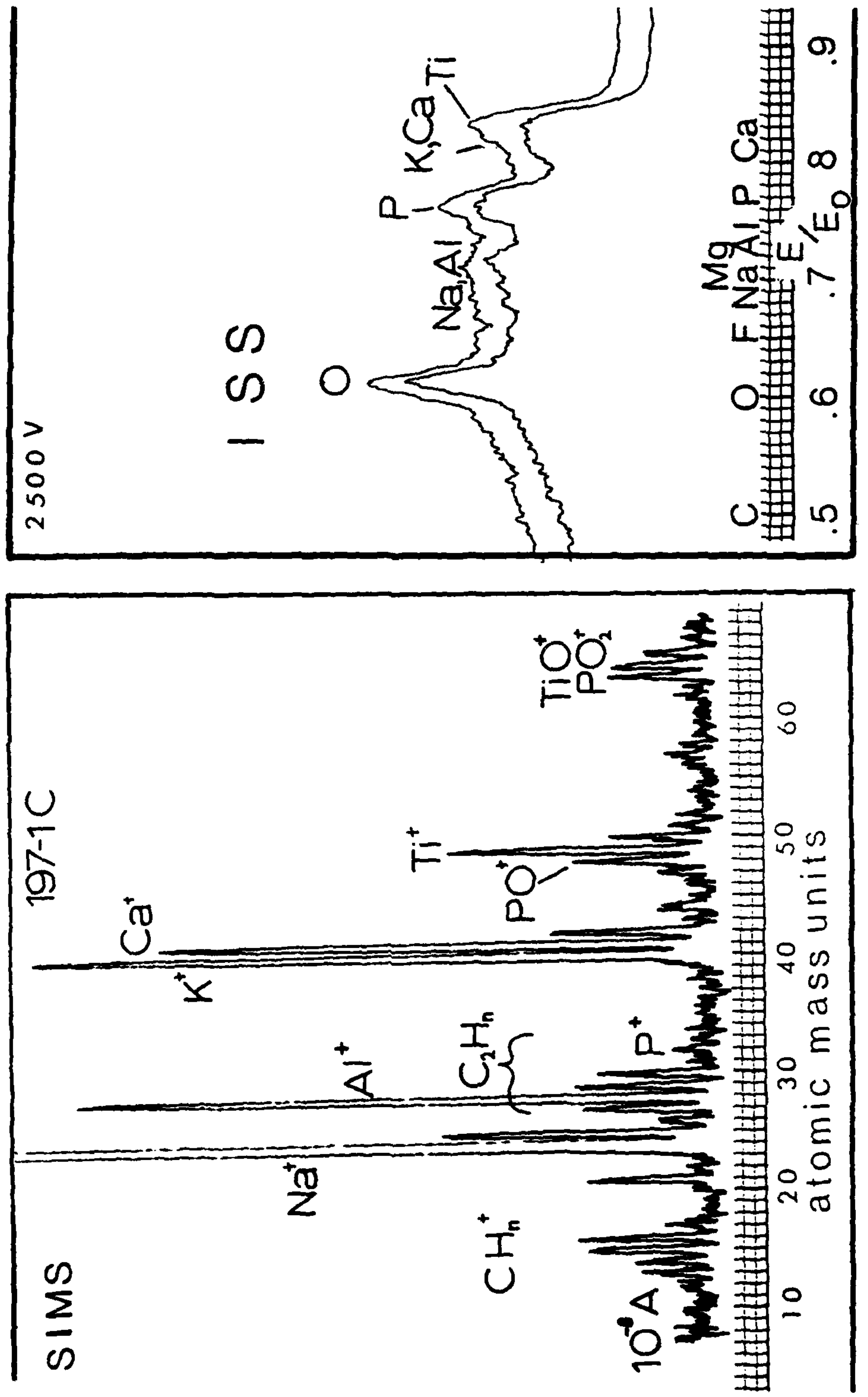

Figure 5. ISS/SIMS Data for Sample 197-1c

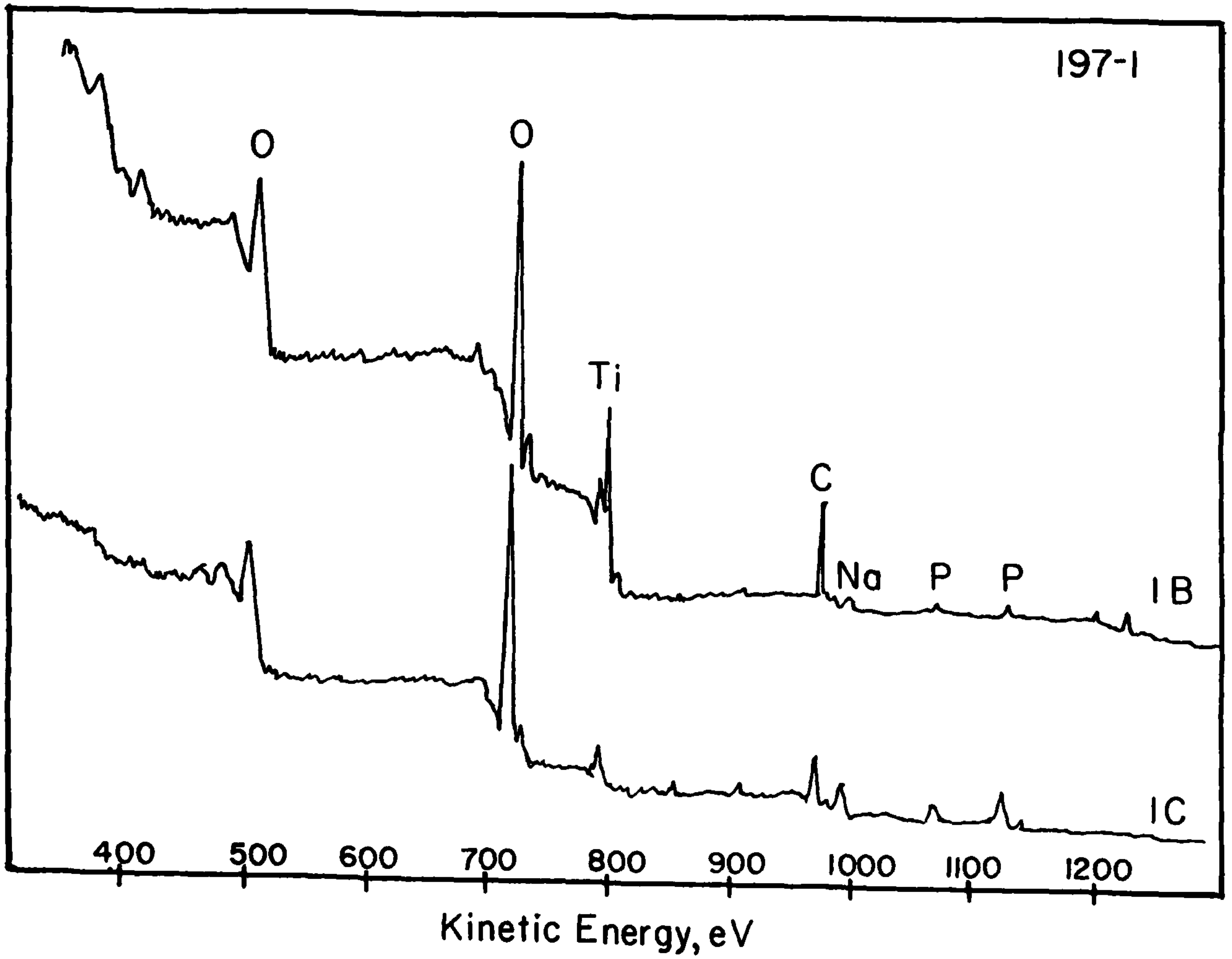

Figure 6. Photo Electron Spectra from Samples 1b and 1c

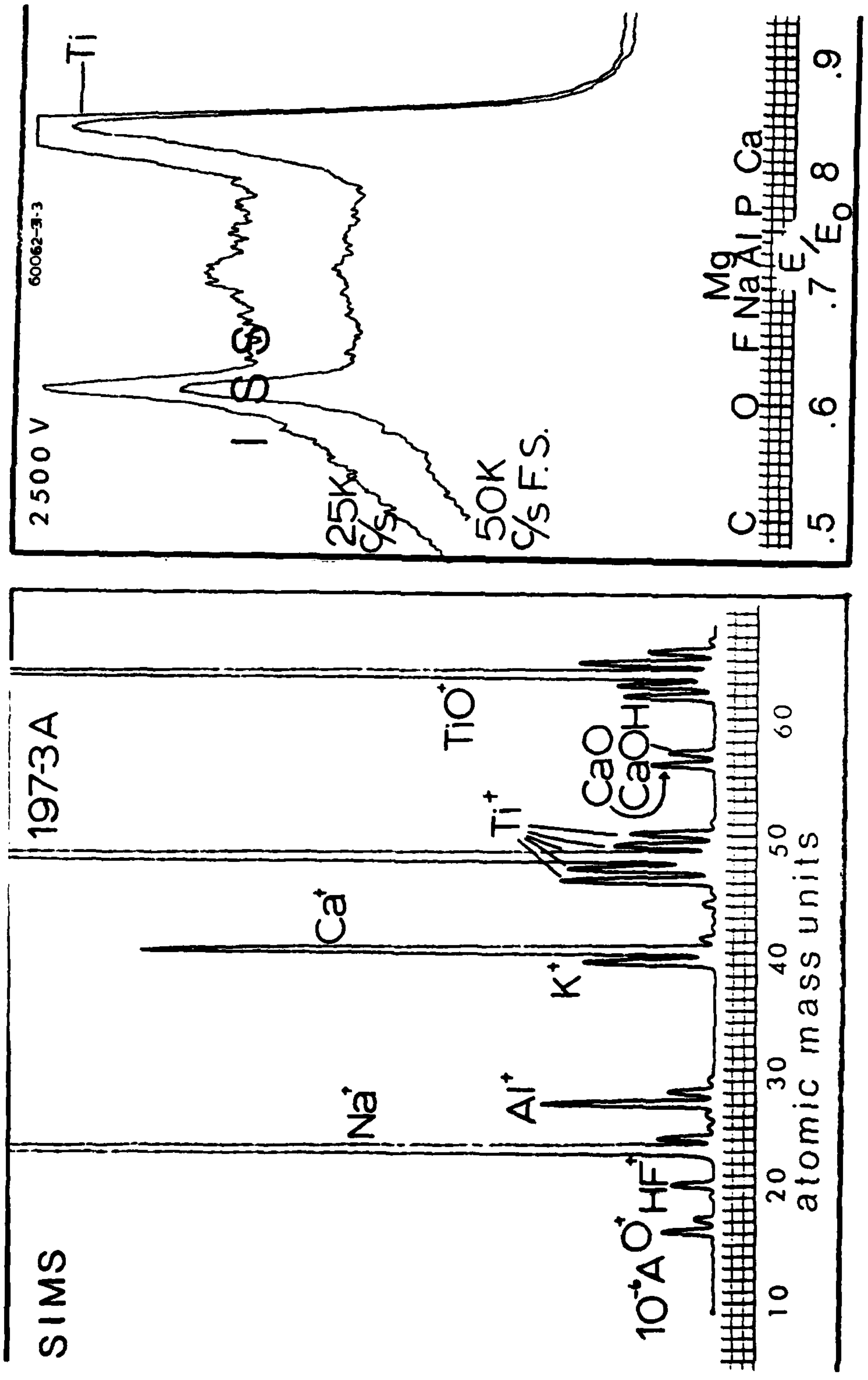

Figure 7. ISS/SIMS Data for Sample 197-3a

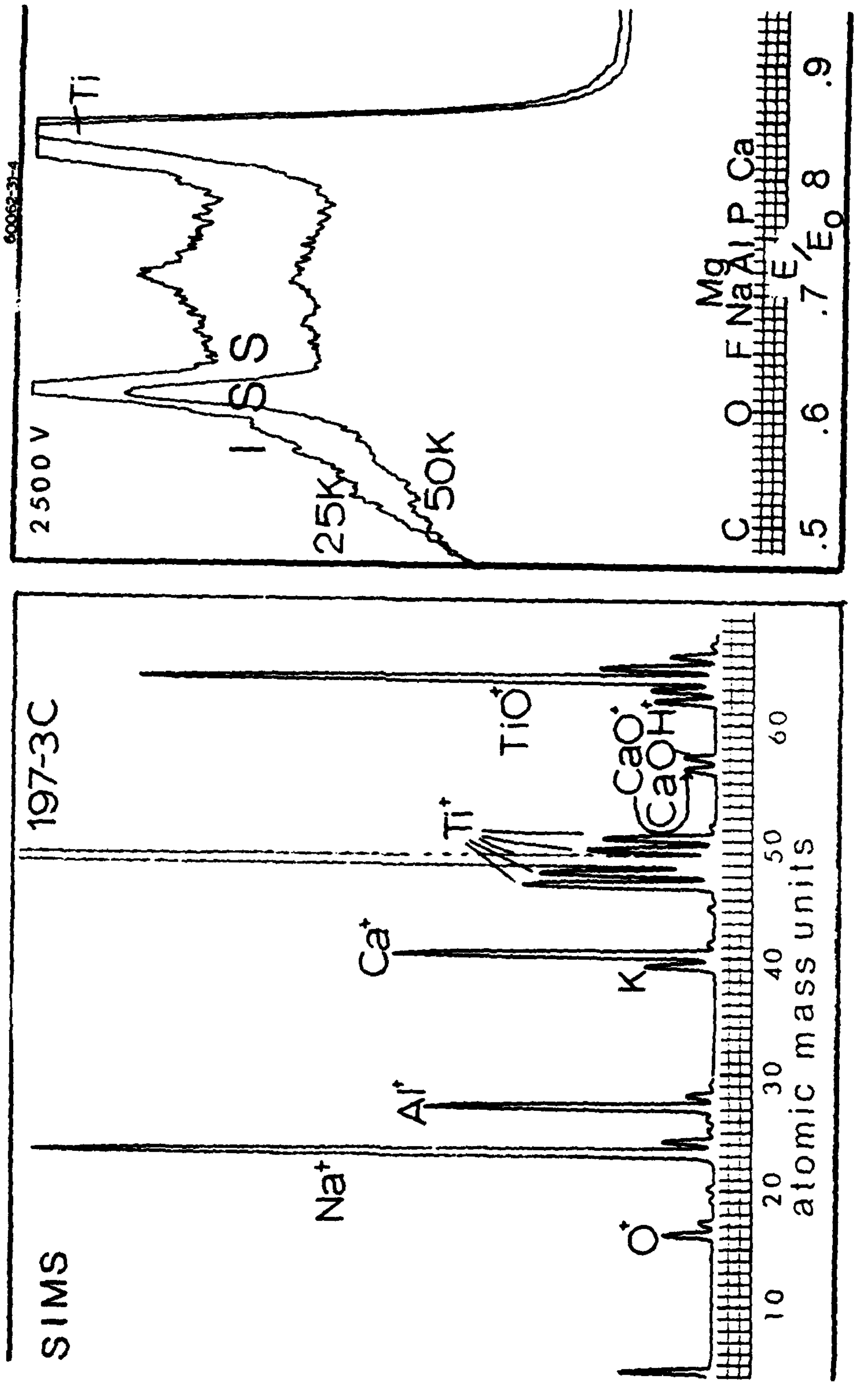

Figure 8. ISS/SIMS Data from 197-3c

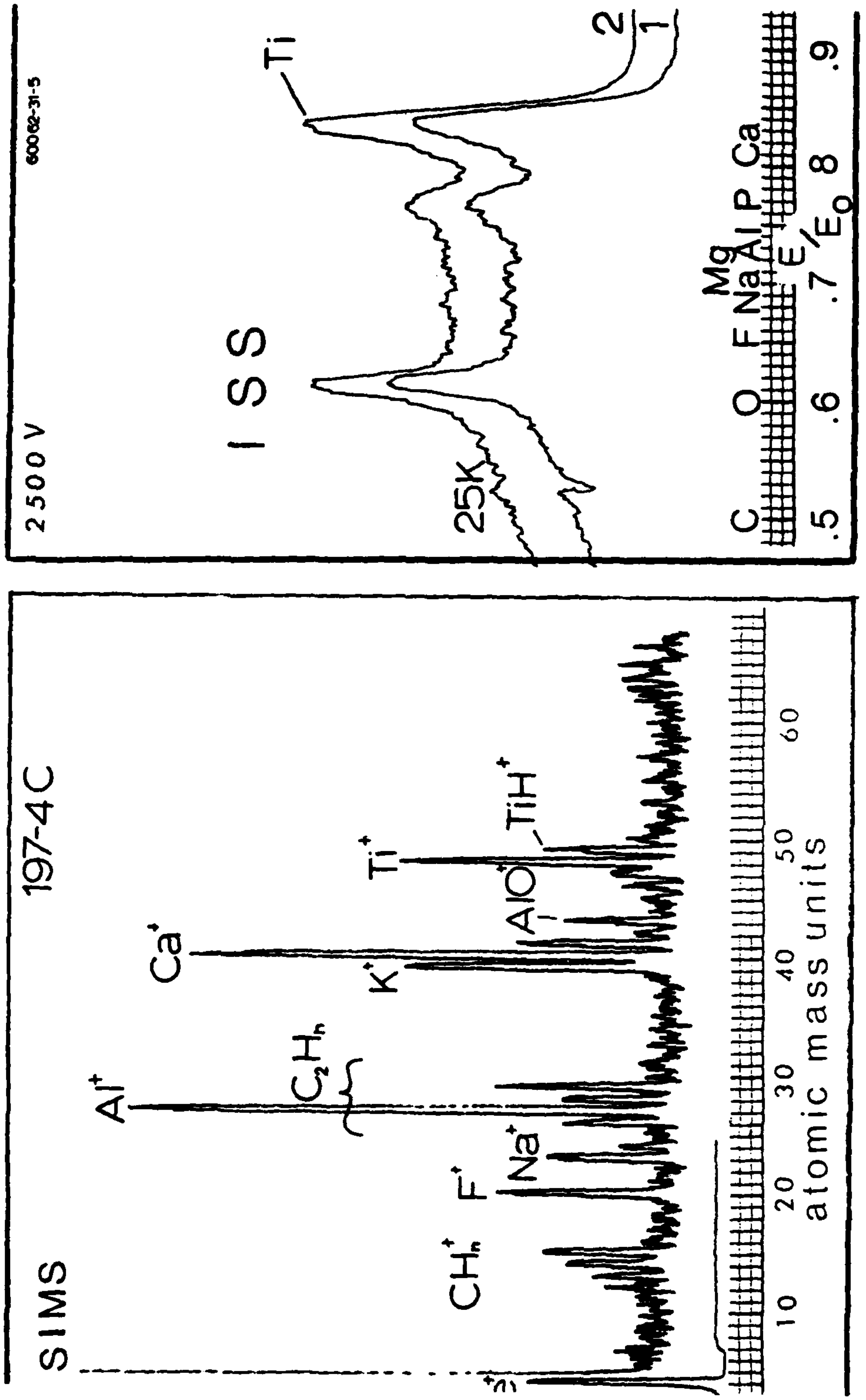

Figure 9. ISS/SIMS Data from 197-4c

electron spectrum of titanium anodized in phosphoric acid is in Figure 10 and shows a large amount of phosphorous to be present in the film. Again the phosphorous, although very high in concentration at the surface, continues on into the film as shown in Figure 11 which is an elemental concentration profile with sputtering time on the anodized titanium. The porous oxide formed in sulfuric acid does not show the impurities seen in oxides produced by electrolytes containing phosphate as in Figure 12 where a typical TiO_2 pattern is observed in the ion scattering spectrum.

Initial bondability of anodized surfaces was tested in the lap shear configuration using numerous commerical epoxy adhesives. With one exception, all surfaces proved to be bondable and gave acceptable lap shear values. That exception was anodized films formed in any electrolyte containing fluorine ions. The result was rather unexpected since commercial patent calls for the addition of fluorine ions to a solution to increase the current density and subsequently the porosity of the anodized film for adhesive bonding. The adhesive showed good adhesion to the oxide film in these cases. Failure often occurred interfacially at the oxide/metal interface. When a test in which pure shear was placed at the interface then failure always took place interfacially at the oxide/metal interface. Peel tests on anodized films in which fluorine was present also showed interfacial failure in most tests. Peel strength in the anodized regions were virtually zero. In anodized films formed in nonfluorine containing electrolytes, however, there was really very little effect due to the anodized film, with properties of the interface primarily dependent upon the pretreatment.

Similarly the H_2O contact angle was affected only very slightly by the dense anodic oxides and the variation of the contact angle could not be correlated with either thickness or the pH of the anodizing solution. Contact angle on anodized films, although larger

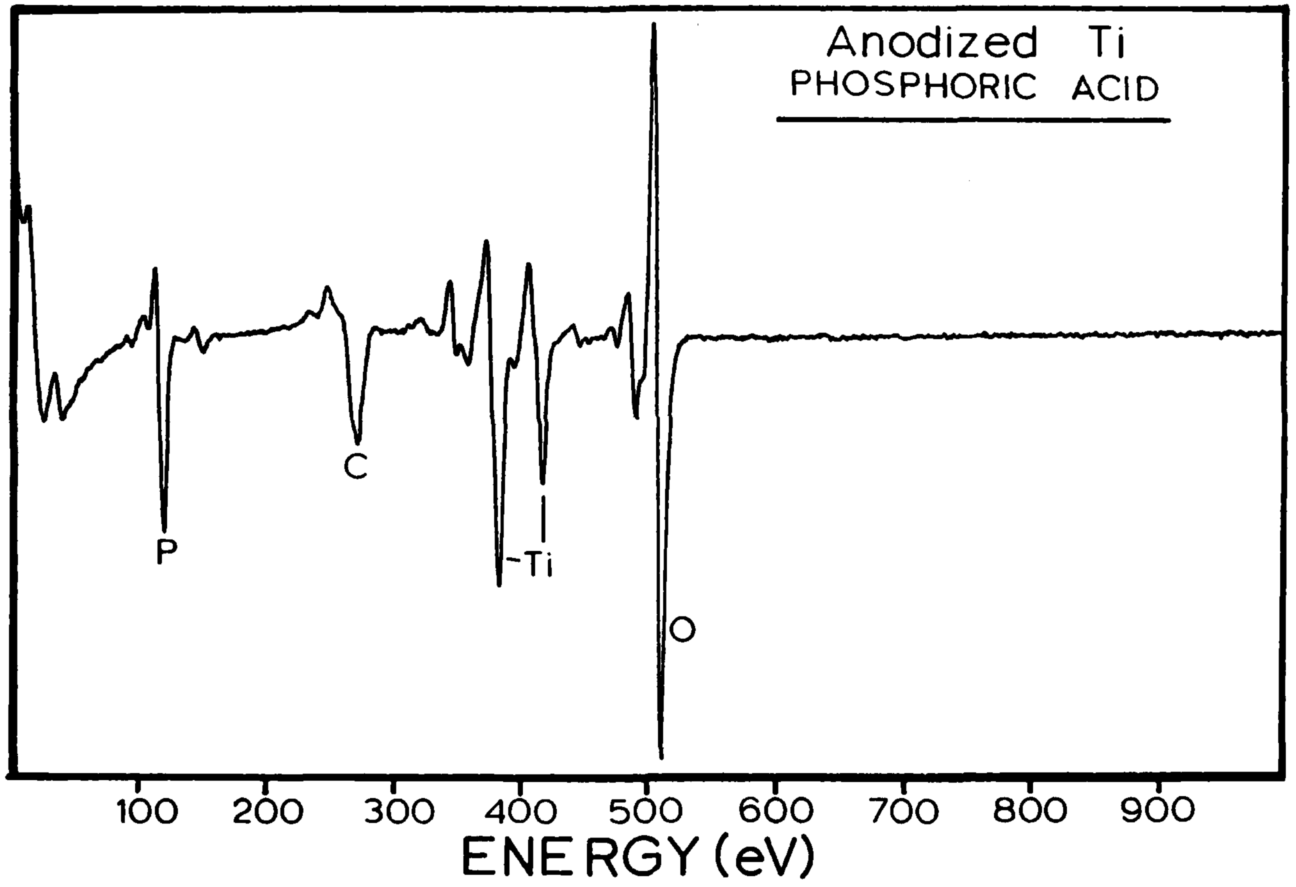

Figure 10. Auger Electron Spectra from Titanium Anodized in Phosphoric Acid

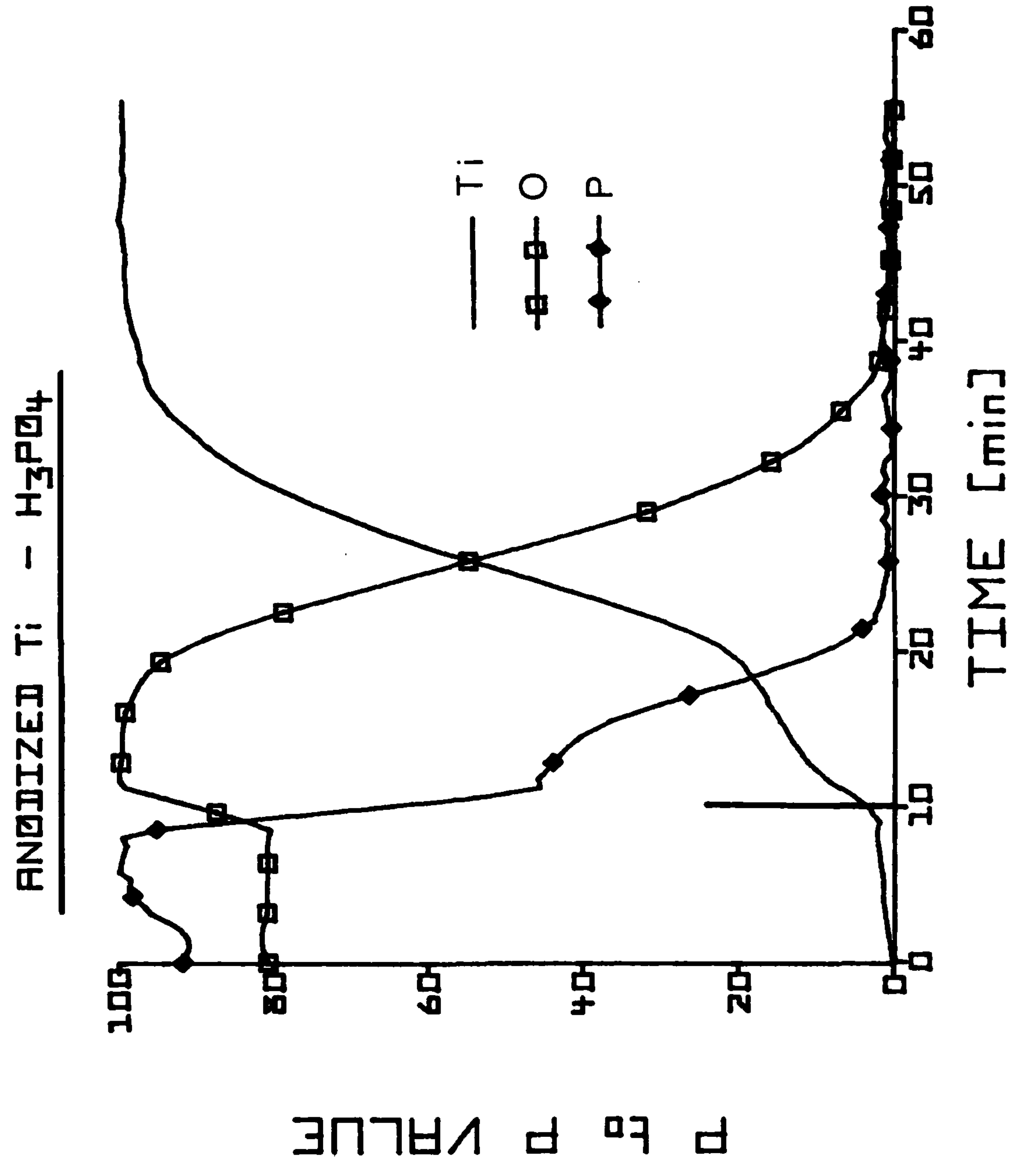

Figure 11. Elemental Depth Profile Obtained by AES on Titanium Anodized in H_3PO_4

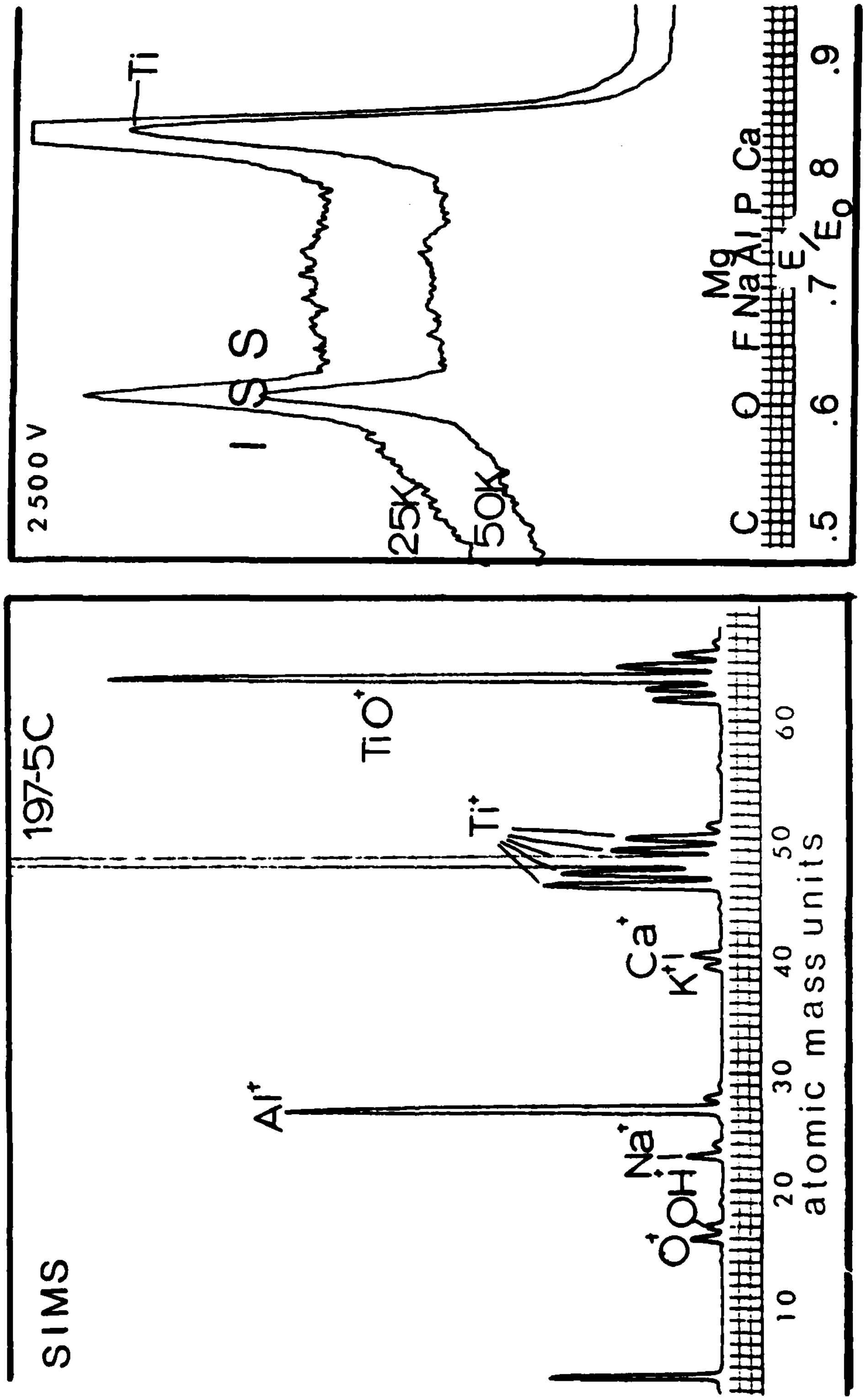

Figure 12. ISS/SIMS Data from 197-5c

than expected, nevertheless was slightly lower in every case than the original etched surface. Contact angle data for several of the dense oxides is shown in Figure 13. It is seen in Figure 14 that the contact angle decreases with increasing thickness and porosity. The most porous film 197-2, shows the lowest contact angle and also exhibits spreading of the drop with time going to almost zero contact angle in ten minutes.

The contact potential, as compared to a vacuum evaporated gold film, was measured on each of the specimens. The contact potential data although showing a good deal of scatter could be correlated directly with thickness as shown in Figure 15. This figure shows the spread of contact potential measurements for each of the categories of specimens prepared in this work. It is found that etches, nonporous anodizations and porous anodizations fall into each of the three classes. Some extremely thick and porous anodized films could not be measured and produced instability in the electrostatic volt meter.

In order to determine the effect of anodization on peel strength, specimens were etched over the entire area and anodized over one half of the specimen surface as shown in Figure 16. The peel curves were obtained as in A where there was little or no affect in the peel strength in the etched or anodized regions. In the area of the anodized oxide at the meniscus there was a drop in peel strength. In other specimens the peel strength dropped somewhat in going from the etched area into the anodized area. As was mentioned earlier in specimens anodized in electrolytes containing fluorine the peel strength dropped to zero at the interface between the etched and anodized areas and the failure mode changed from cohesive to interfacial at the oxide/metal interface.

3. CHEMICAL TREATMENTS

Table 4 shows the sample treatment that was used for the remainder of the unanodized specimens and the treatments are shown

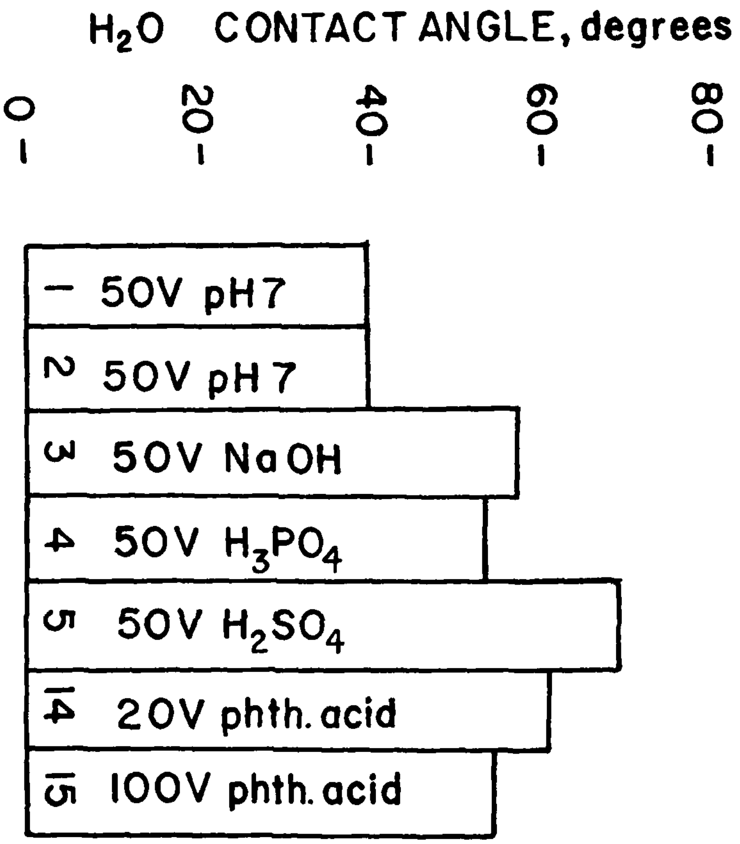

Figure 13. H_2O Contact Angle for Anodized Films

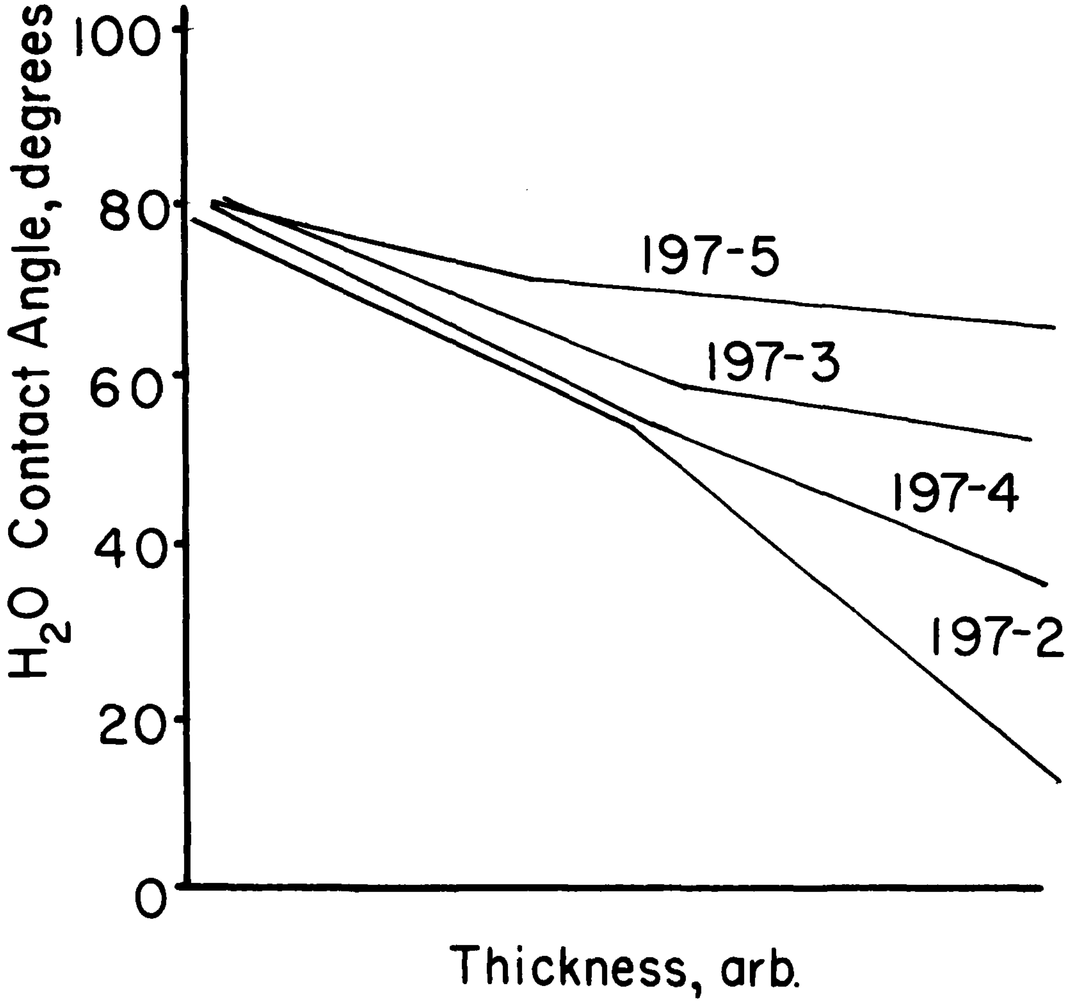

Figure 14. H_2O Contact Angle for Increasing Thickness of Anodized Films

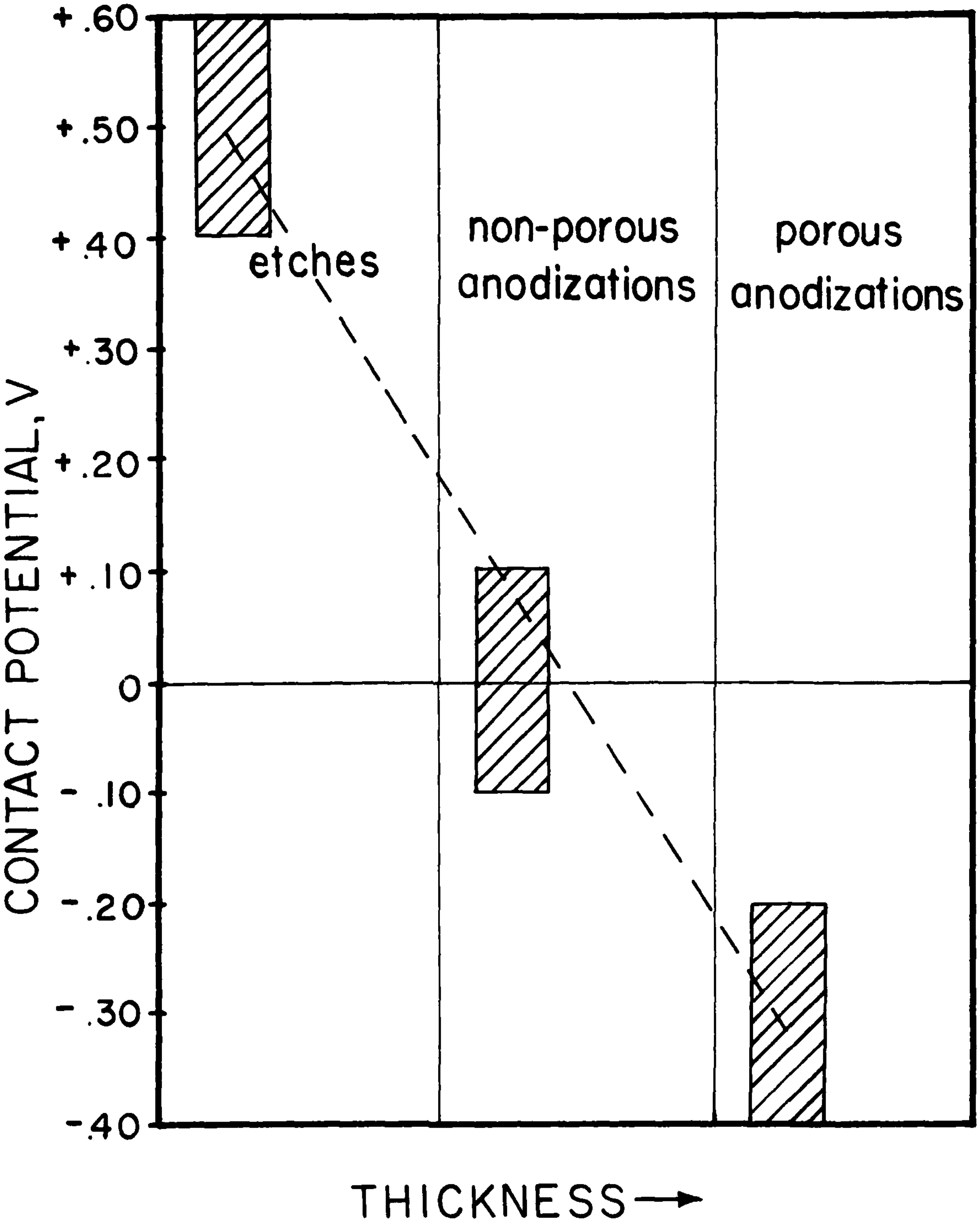

Figure 15. Contact Potential for Oxide Films Formed on Ti6Al4V

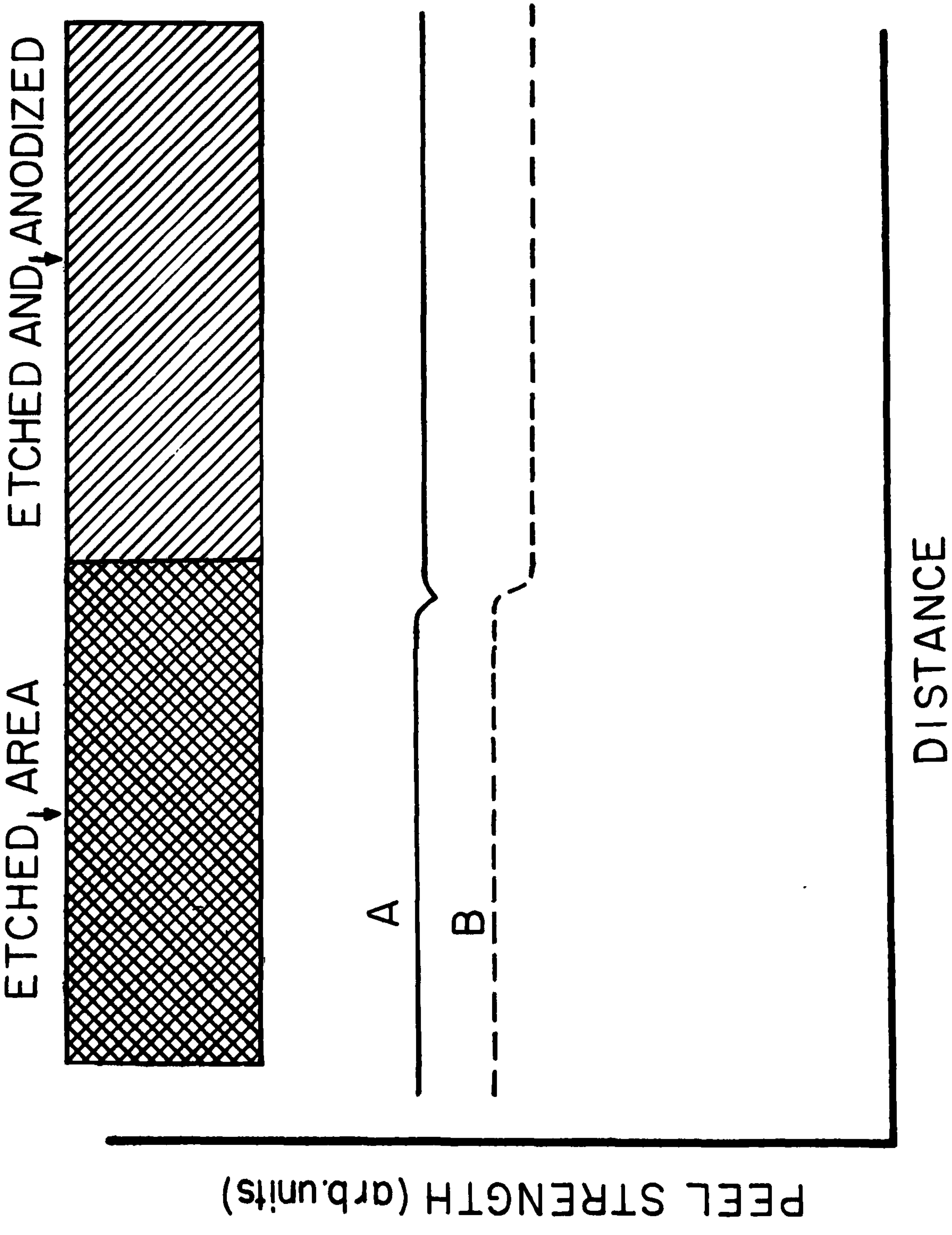

Figure 16. Typical Peel Results from Etched and Etched and Anodized Ti6Al4V

by number with the explanation of the treatment which pertains to each number. Some of the treatments are very similar but have a difference of only one step. For instance in 197-6 and 197-7, the pre-etch is different. As can be seen by Figures 17 and 18, the two surfaces are virtually identical as would be expected. The surface composition being apparently highly dependent on the final conversion step. Note, however, one interesting minor difference in chemistry in the two surfaces as shown in the SIMS spectra. Specimen 197-6, following the first etch was washed in tap water while specimen 197-7 was washed in deionized water. It can be seen in Figure 17 that appreciable amounts of calcium continue to remain on the surface apparently from the tap wash water while no calcium is detected on specimen 197-7. Note also the large amounts of TiF+ as compared to TiO+ present on these surfaces suggesting that the conversion coating is perhaps either a complex oxy fluoride or a structure in which many vacancies exist and fluorine and sodium exist interstitially with the positive and negative charges maintaining charge neutrality. The Auger spectrum as seen from 197-6 in Figure 19 are the same elements that were determined by SIMS.

The ISS/SIMS spectra from sample 197-8 is shown in Figure 20. This specimen was given the same treatment as specimen 197-7 but with a different final modification step. Following conversion, this specimen was boiled in deionized water for 30 minutes. Notice that it has changed considerably with the ISS spectrum taking on the characteristics of TiO_2 shape. The SIMS spectra is likewise very different with virtually all traces of fluorine having disappeared during this treatment. Also, it may be of importance that the apparent concentration of the vanadium with reference to titanium has increased during this modification step. Such an increase in vanadium content is also seen in high temperature corroded specimens of titanium-6aluminum-4vanadium.

Specimen 197-9 (Figure 21) was given another modification step (heating the specimen to 900°F) which diminishes the fluorine but does

TABLE 4

SAMPLE TREATMENT

Sample	Treatment
197-1 thru 5	As shown in Table I
197-6	1, 2, 8, 2, 10, 3, 4
197-7	1, 2, 9, 3, 10, 3, 4
197-8	1, 2, 9, 3, 10, 3, 4, 6, 5
197-9	1, 2, 9, 3, 10, 3, 4, 7
197-10	1, 2, 8, 2, 4
197-11	1, 2, 8, 3, 5
197-12	1, 2, 8, 2, 11, 3, 4
197-13	1, 2, 8, 3, 4, 6, 5
197-14	1, 2, 8, 3, 12 (20V), 3, 4
197-15	1, 2, 8, 3, 12 (100V), 3, 4

1. Abrasive pad + detergent
2. Tap H_2O
3. Deionized H_2O
4. Wipe (paper towel)
5. Drain dry
6. Boil in deionized H_2O
7. Heat to 500°C
8. H_2SiF_6, 5%, 50°C
9. HF/HNO_3, 40ml/360ml to make 1 liter
10. $HF/NaF/Na_3PO_4$, 26ml/99/50g to make 1 liter
11. H_2SO_4 (0.1M)
12. Anodization - phthalic acid, 2g/1 H_2O

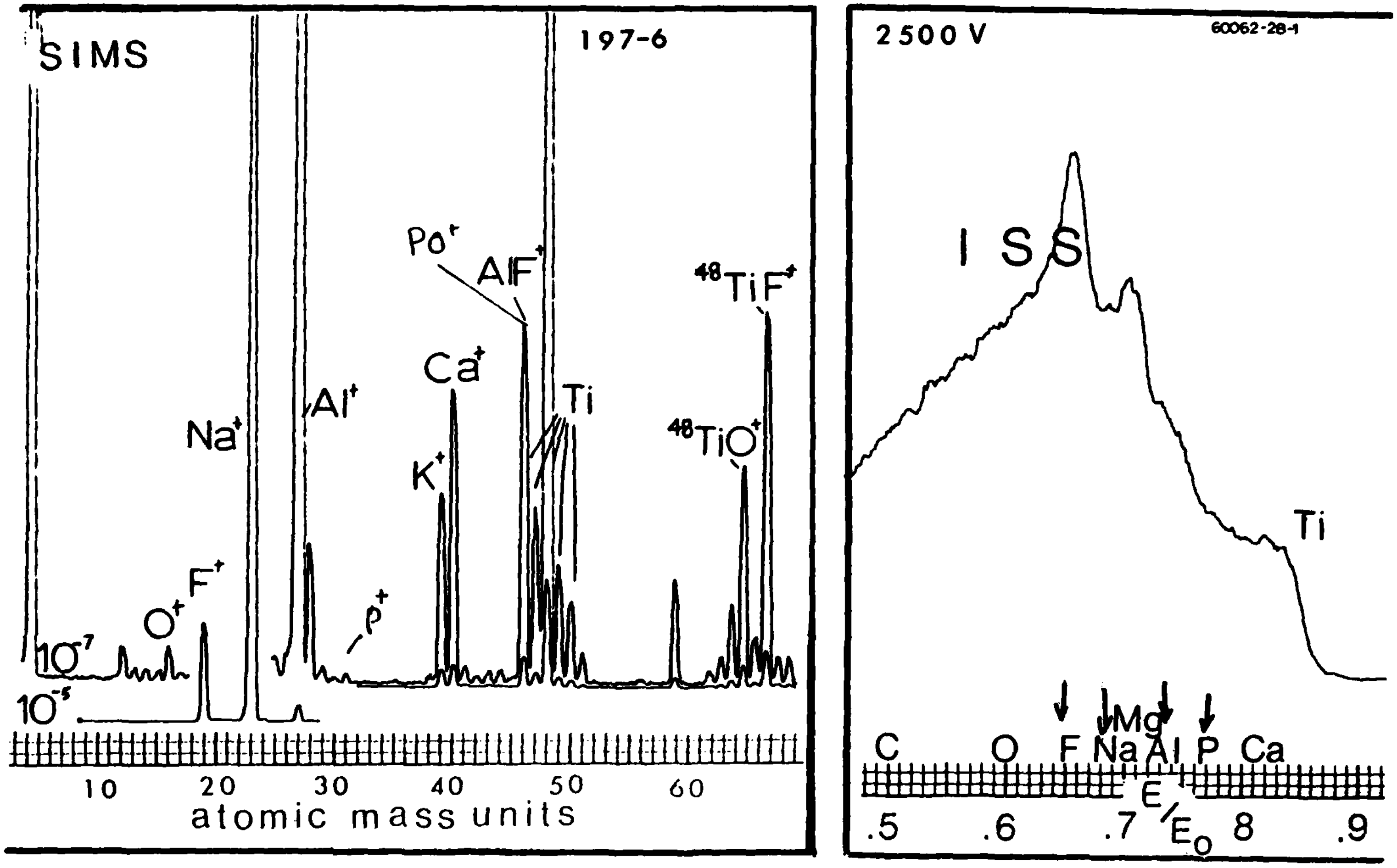

Figure 17. ISS/SIMS Data from 197-6

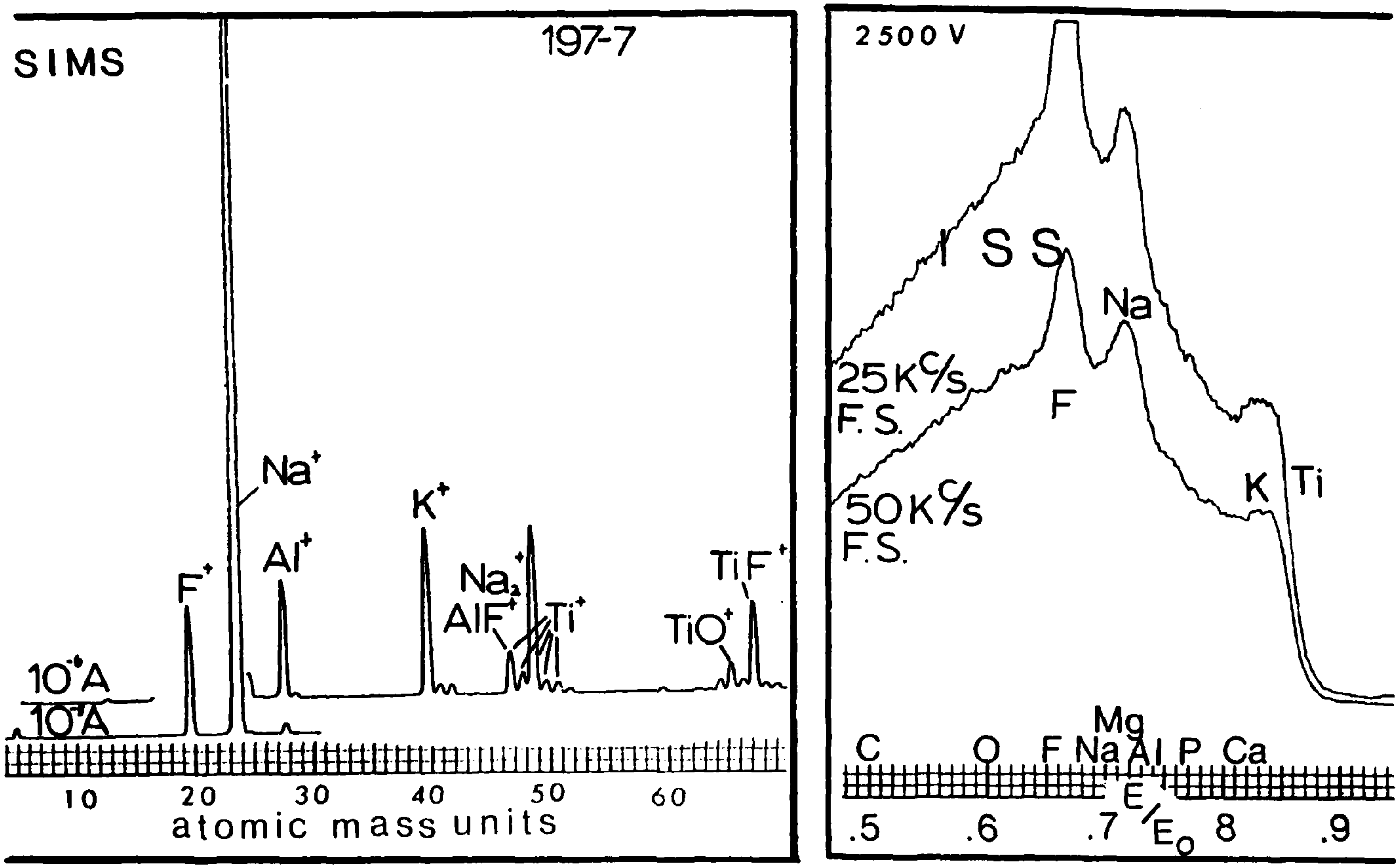

Figure 18. ISS/SIMS Data from 197-7

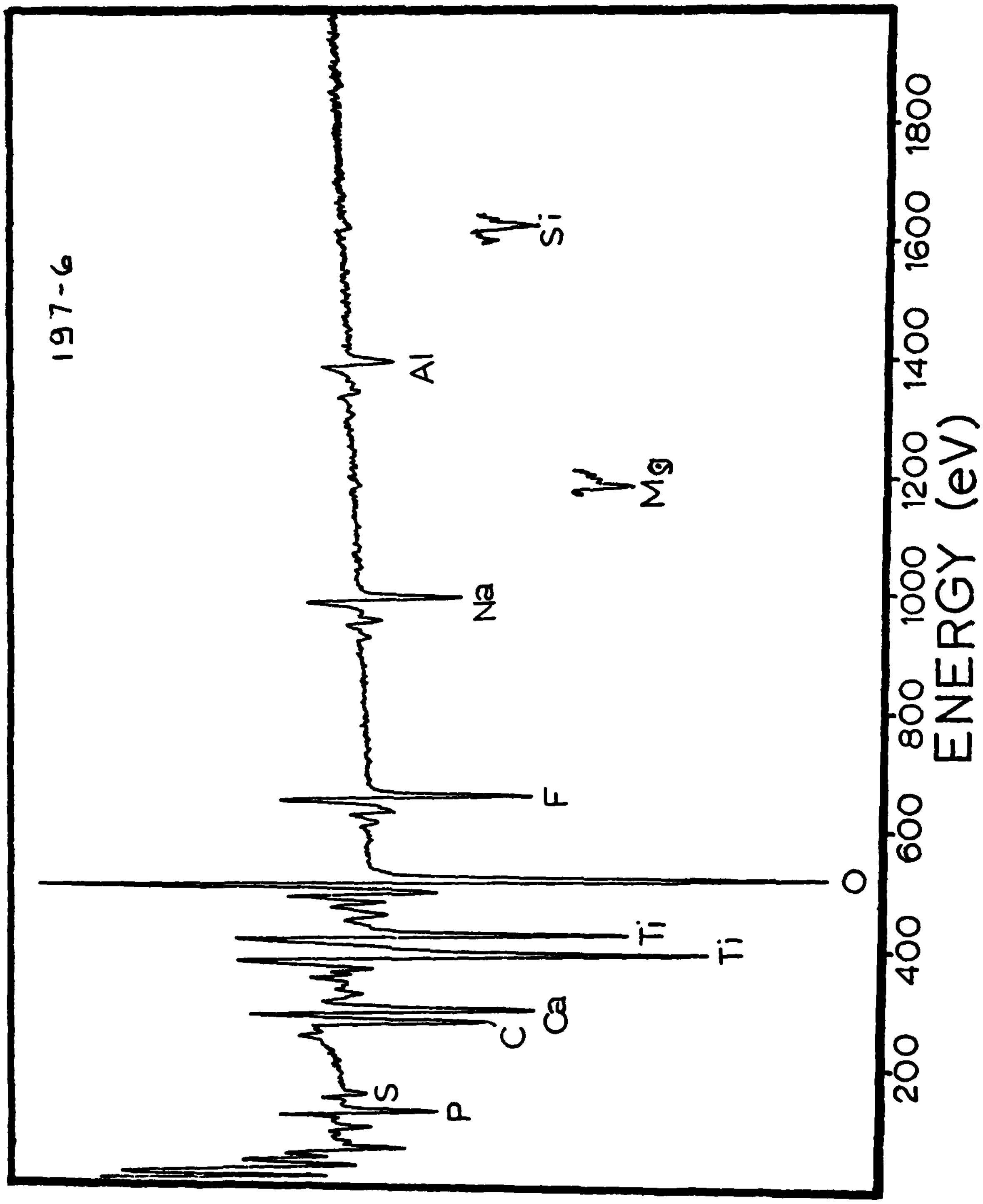

Figure 19. AES Data from 196-6

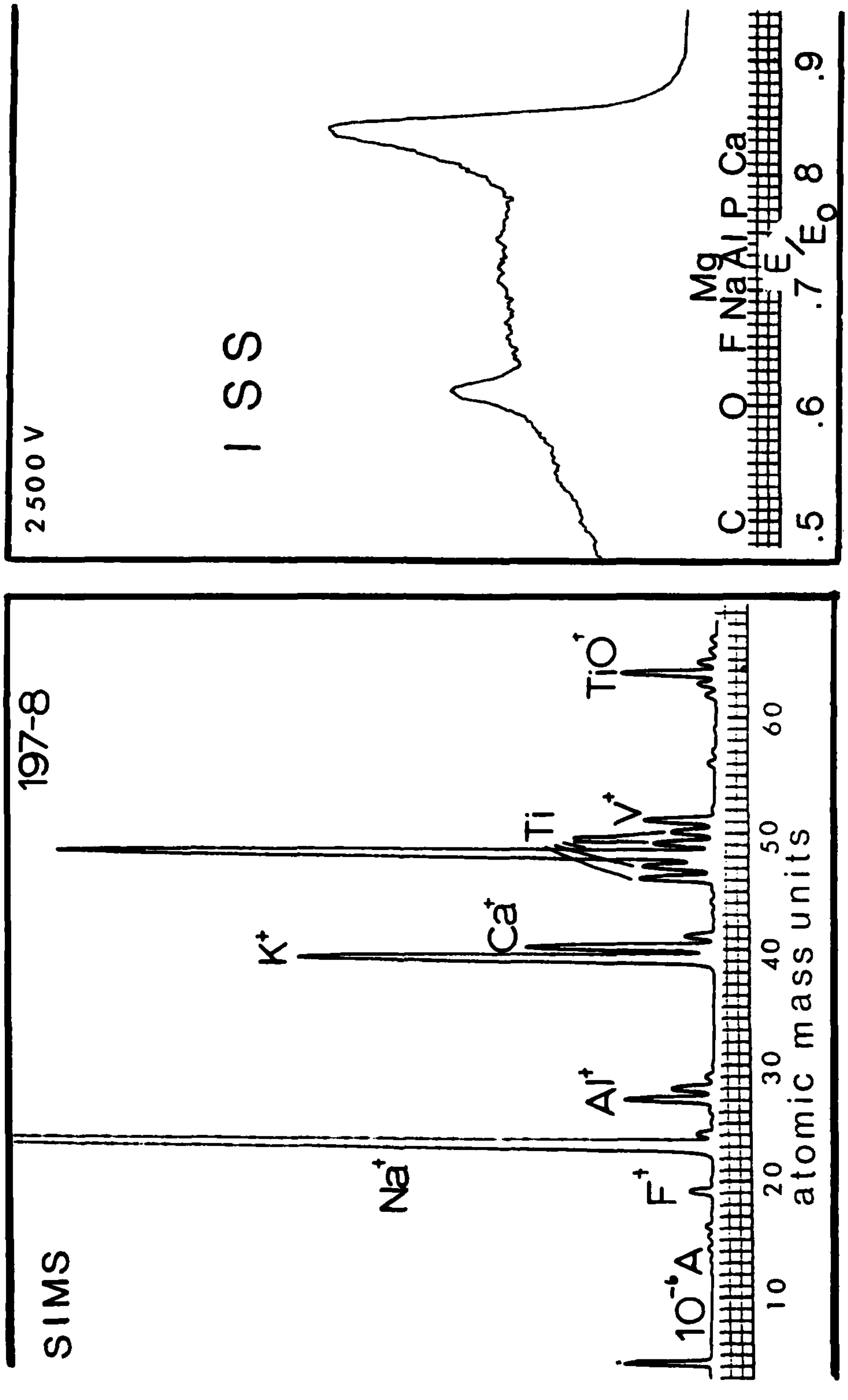

Figure 20. ISS/SIMS Data from 197-8

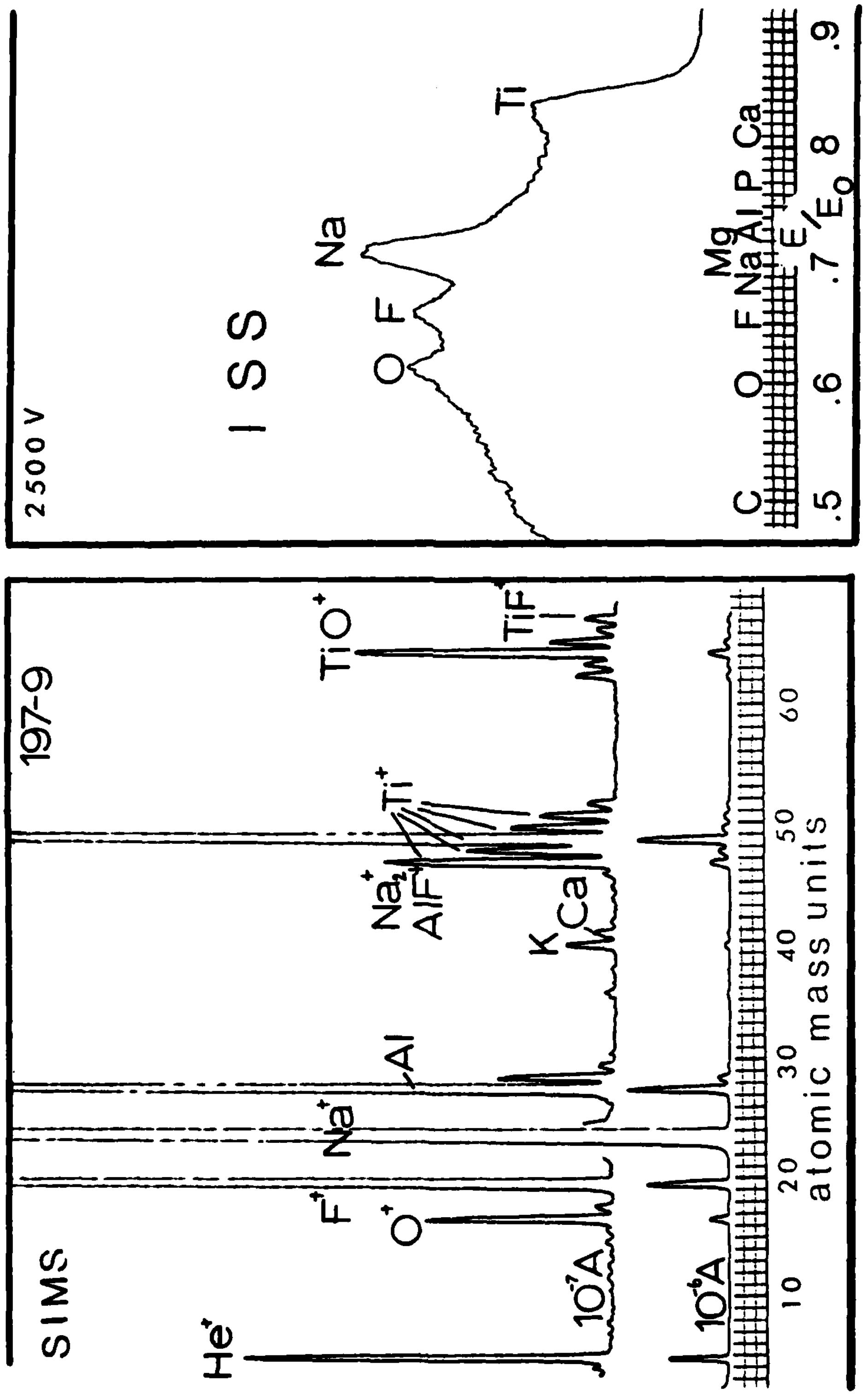

Figure 21. ISS/SIMS Data from 197-9

not completely remove it. In addition there is a large increase in sodium concentration at the surface. This is typical of many materials which contain sodium and potassium in trace quantities. When the sample is heated these alkali elements apparently diffuse to the surface by grain boundary migration. Even specimens heated to much more moderate temperatures, such as the temperatures common in adhesive bonding, show some sodium diffusing to the surface. Frequently when true interfacial failure of adhesive bonds is observed, the surfaces of both the adherend and adhesive show large amounts of alkali elements.

Contact angle and contact potential were measured on each of the specimens which were etched and given a conversion treatment along with some modifications. The contact potential showed virtually the same potential for each of the specimens as shown in Figure 22. However, the contact angle showed appreciable differences especially in specimen 197-9 where the contact angle dropped to near zero. This is also typical of many materials which are heated. The apparent diffusion of the alkaline elements to the surface causes a drop in contact angle and the formation of a very wettable surface. Contact potential and contact angle were also measured for some of the anodized films and are shown in Table 5. Table 6 shows the affect of heat and humid age on contact potential and contact angle on anodized oxides. This set of specimens is not from the 197 series and the contact potential and contact angles are not the same as measured in the 197 series. The trend shown in this table is that the contact angle always decreases upon heating of the specimen. When this specimen which was heated was then exposed to humid aging conditions the contact angle increased. Contact potential measurements showed no definite trend although it does seem very sensitive to the thickness of the oxide film and somewhat dependent on the chemistry.

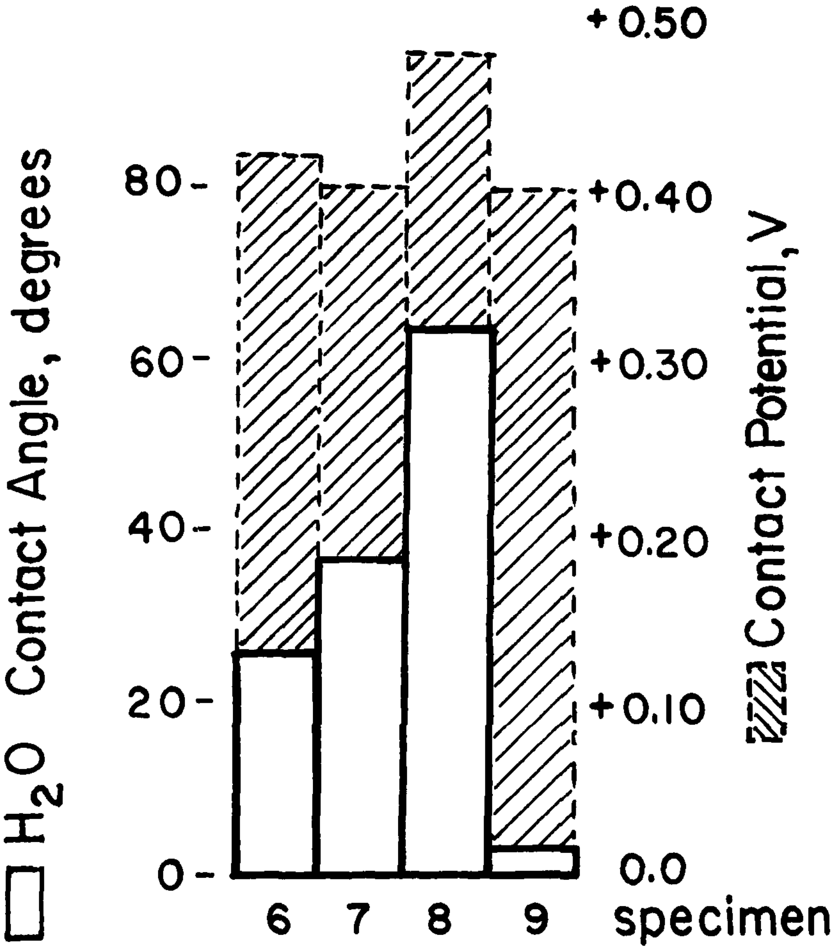

Figure 22. H_2O Contact Angle and Contact Potential for Etched and Etched and Modified Specimens

TABLE 5

CONTACT POTENTIAL AND H_2O CONTACT ANGLE FOR ANODIZED Ti6Al4V

		Anod. V	Contact Pot.V	Contact angle,°
197-1		0V	0.50	78°
Na_2HPO_4	A	20V	0.40	74°
H_3PO_4	B	50V	0.06	57°
pH = 7	C	100V*	0.20	14°
197-3		0V	0.82	80°
0.1M	A	20V	0.36	72°
NaOH	B	50V	0.12	58°
pH = 12.4	C	200V*	0.07	53°
197-4		0	0.86	79°
0.1M	A	20V	0.44	60°
H_3PO_4	B	50V	0.18	54°
pH - 1.80	C	250V*	0.58	36°

* Sparking

TABLE 6

THE EFFECT OF HEAT AND HUMID AGE ON CONTACT POTENTIAL AND CONTACT ANGLE ON ANODIZED OXIDES ON Ti6Al4V

Anodizing Media	Oxide**	As Prepared		Exposure to 392°F (200°C)		Exposure to 200°C Followed by Humid Age	
		C.P,V	$\theta,^{\circ}$	C.P,V	$\theta,^{\circ}$	C.P,V	$\theta,^{\circ}$
Acid	Thin	0.42	33	-0.22	24	-0.20	42
0.1MH_3PO_4	Thick	-0.20	11	-0.42	11	-0.18	38
Neutral	Thin	0.14	43	-0.32	30	-0.16	60
$Na_2HPO_4+H_3PO_4$	Thick	-0.20	12	-0.46	12	-0.04	43
Base	Thin	0.32	44	-0.22	31	-0.18	51
0.1M NaOH	Thick	-0.12	40	-0.30	15	-0.04	51

*Humid age at 160°F (71°C) 95% R.H.

**Thin oxide 50V

Thick oxide, porous with sparking

Figures 23 and 24 show specimens etched in hydrofluosilicic acid. Note that although fluorine is present on these surfaces it is not nearly as concentrated and does not show an indication of chemical combination as in the chemical conversion coatings formed from fluorides in the earlier spectra. Specimens 197-12 (Figure 25) etched in sulfuric acid shows the formation of a typical TiO_2 film. Heating of a H_2SiF_6 etched surface produces large amounts of sodium shown in Figure 26. Spectral data for the last two specimens is shown in Figures 27 and 28 for a thin and relatively thick anodized film obtained from an organic acid solution. Note here in the SIMS spectra the very great intensity of TiO^+ as compared to Ti^+.

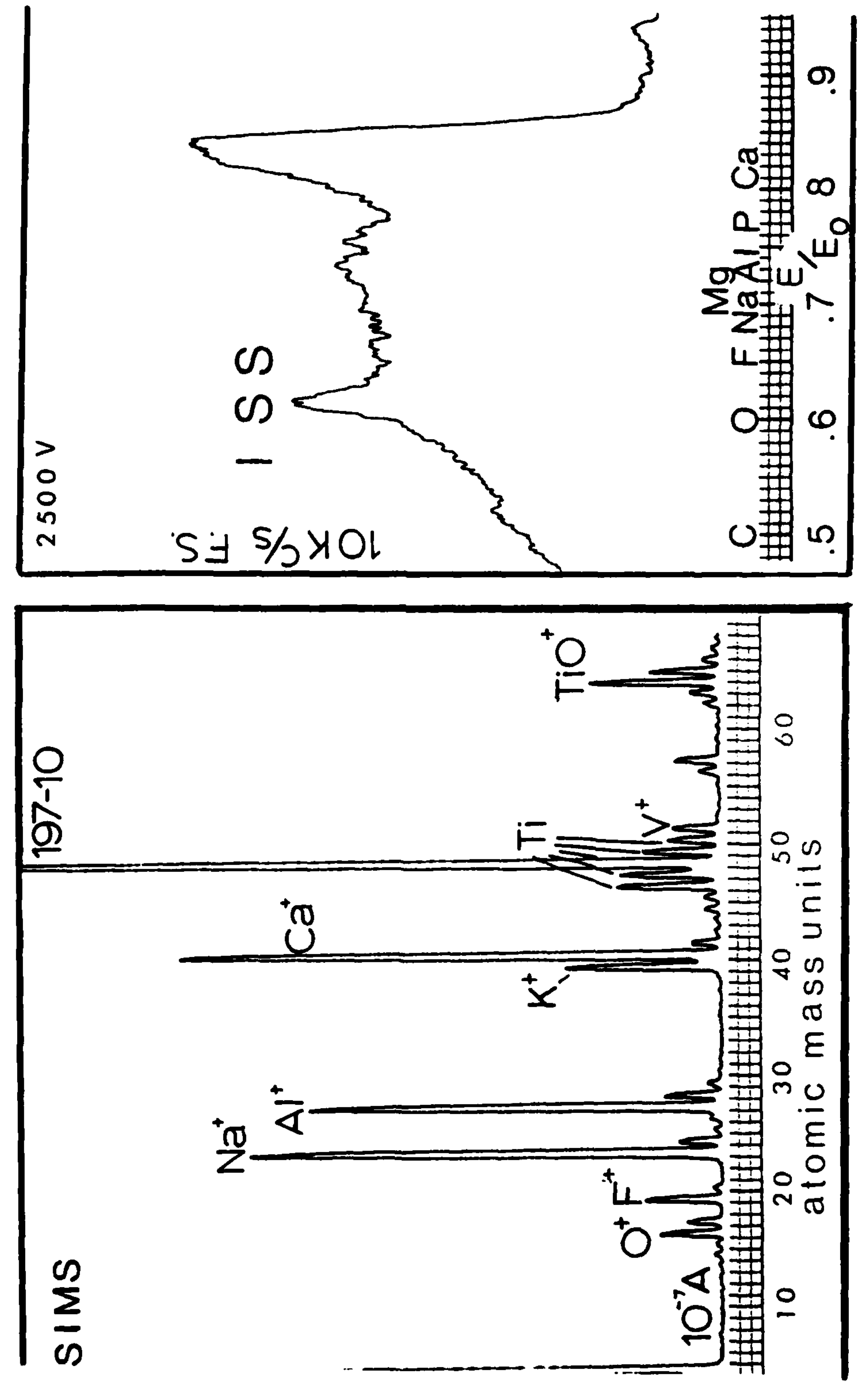

Figure 23. ISS/SIMS Data from 197-10

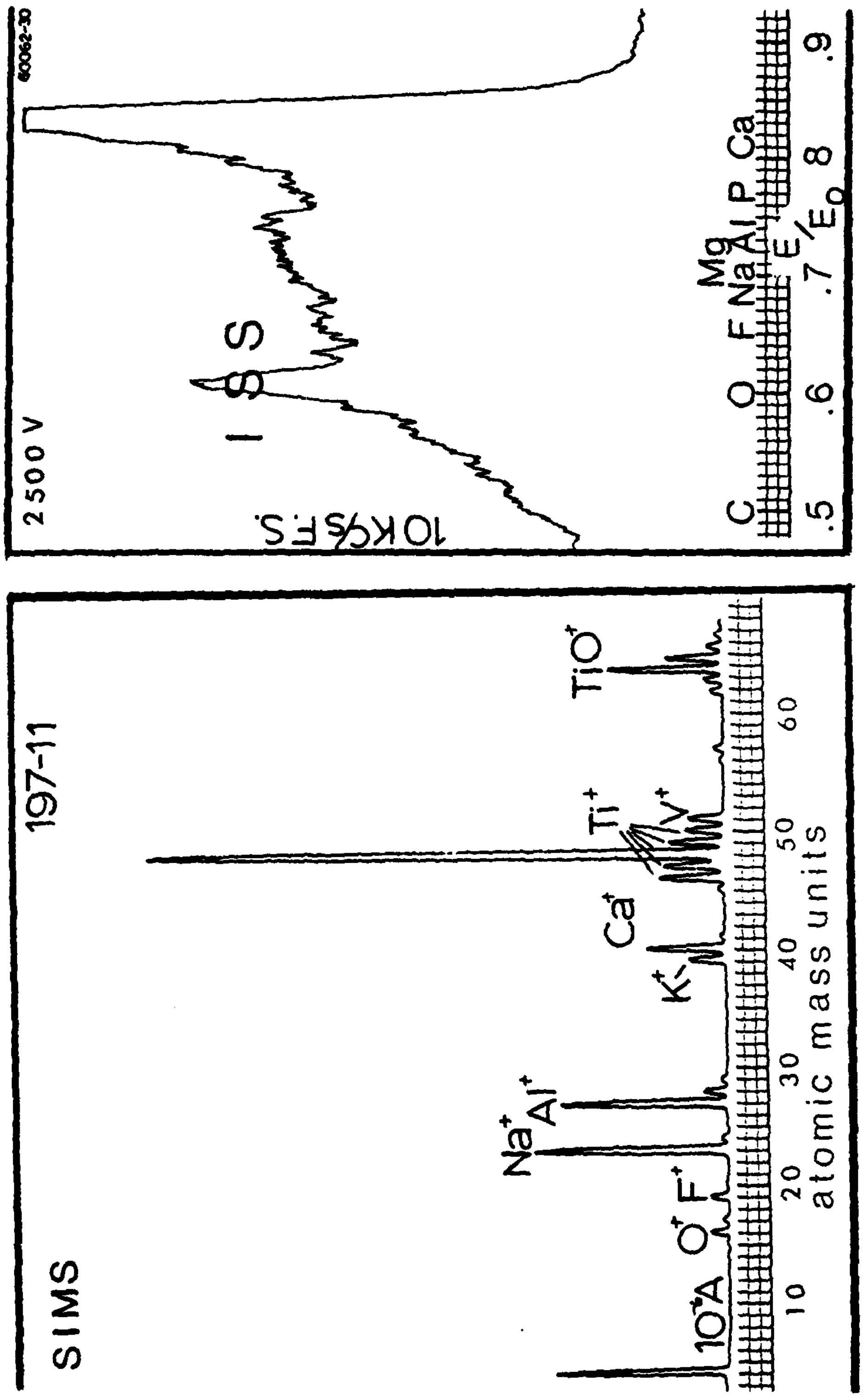

Figure 24. ISS/SIMS Data from 197-11

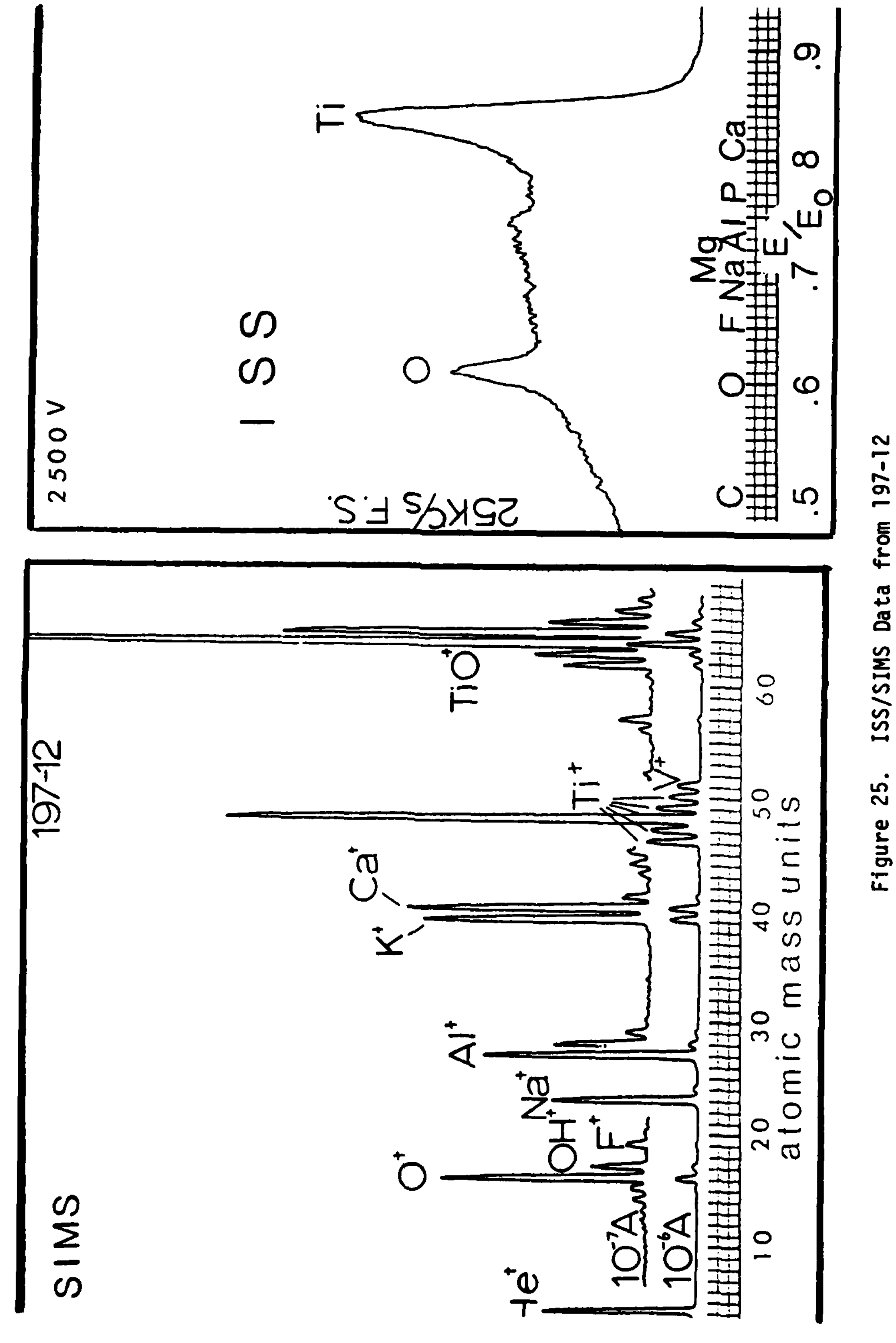

Figure 25. ISS/SIMS Data from 197-12

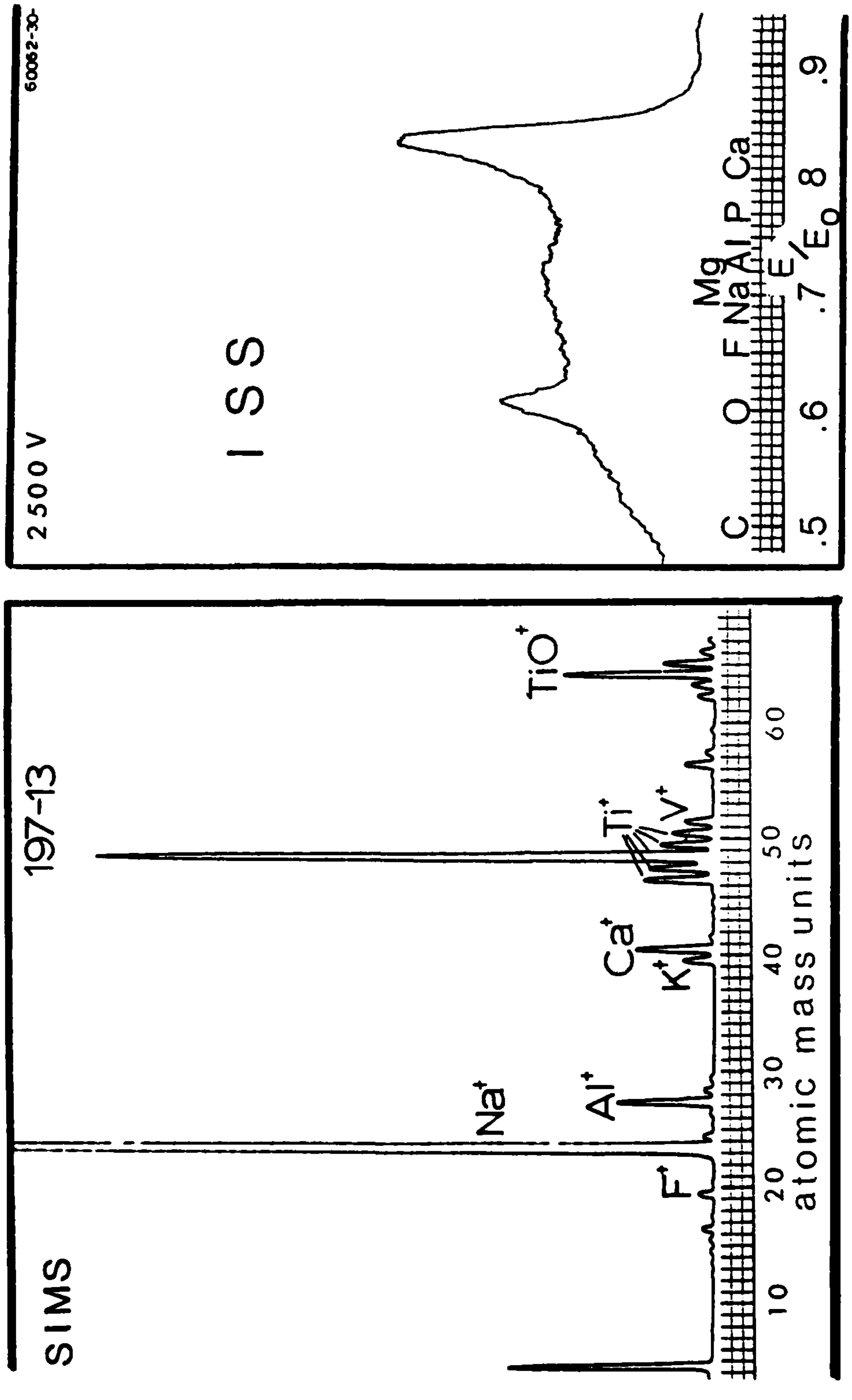

Figure 26. ISS/SIMS Data from 197-13

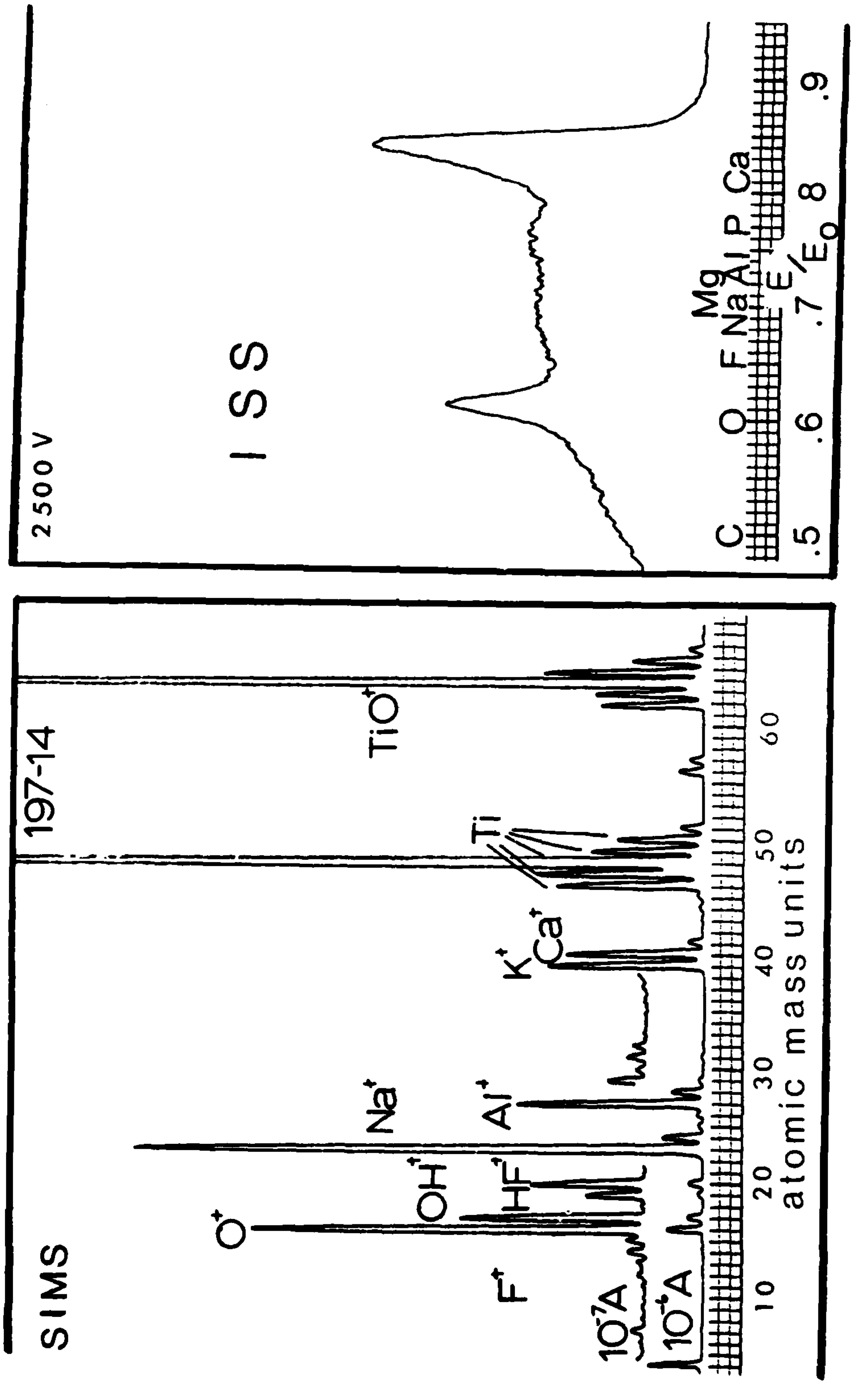

Figure 27. ISS/SIMS Data from 197-14

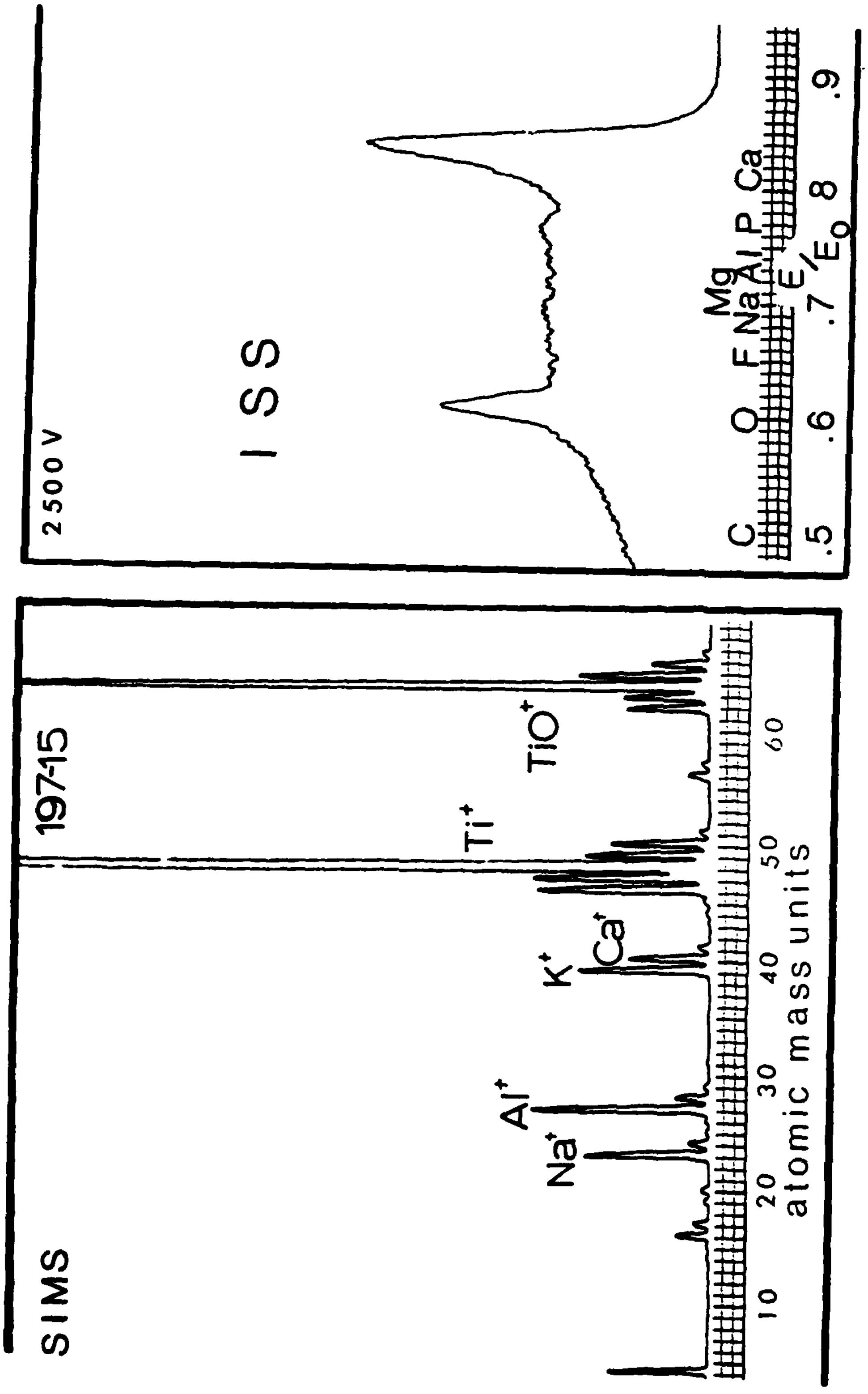

Figure 28. ISS/SIMS Data from 197-15

SECTION IV

CONCLUSIONS

Large changes in surface chemistry are seen with changes in surface preparations. Similarly, surface morphology is very dependent on the preparation method. Initial adherence of epoxy base adhesives to Ti6Al4V appears to be very sensitive to morphology but only slightly dependent on subtle changes in chemistry. Chemistry of surfaces seems to be more important in consideration of long time durability and the destructive ingress of water vapor. The formation of dense anodic oxides does not seem to influence bondability appreciably and in some cases actually lowers bond strength. When fluorine is present in the anodization bath a weak boundary layer is formed which causes the oxide to "unzip" from the metal. Anodization does, however, provide a highly uniform oxide which under certain conditions may be beneficial for adhesive bonding. Perhaps for very high temperature processing and use, the anodized film will provide a diffusion barrier and impede further oxidation of the surface.

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APPENDIX A

ION SCATTERING DATA 90° SCATTERING

ELEMENT			E/E_0 (at $\theta = 90^\circ$)			
Z	A		^3He	^4He	^{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	A1	.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	C1	.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	. 75
49	114.8	In	.949	.933	.703	.483
50	118.7	Sn	.951	.935	.712	.496

APPENDIX B

RELATIVE ABUNDANCES OF NATURALLY OCCURRING ISOTOPES

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	01																		
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		003		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												15.8		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

*U.S.Government Printing Office: 1980 — 657-084/544

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