An introduction of various spectroscopic methods to identify *in vivo* metal wear in total knee arthroplasty

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Received 5 January 2006; revised 11 August 2006; accepted 4 May 2007
Published online 8 August 2007 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jbm.a.31507

Abstract: While the industrial community already employs multiple surface analytical techniques to study compositional wearing of various metallic and nonmetallic materials, as yet, these methods have not been widely introduced into the biological community. We report on a novel approach, using the industrial spectroscopic techniques of X-ray photoelectron spectroscopy, micro-Raman spectroscopy, and scanning electron microscopy equipped with energy dispersive spectroscopy, to identify the fine wear particulates and other impurities deposited within the knee-joint following total knee arthroplasty. In this study, synovial fluid was extracted from knee-joints scheduled for revision of total knee arthroplasty. The small debris flake formed by centrifugation of the fluid was analyzed using the spectroscopic techniques mentioned above. These nondestructive techniques were successful in identifying numerous micron and submicron sized metallic particulates that appear to emanate from both the prosthetic bearing (articulating) surfaces and from backside (nonarticulating) surfaces, even when gross wearing of the prosthetic device was not detectable by direct visual inspection intraoperatively. Most interesting is that the ratio of the *in vivo* metallic debris is approximately the same ratio as that of the manufactured alloy, indicating prosthetic wearing as opposed to chemical dissolution. More importantly, using these spectroscopic techniques to probe both the surface and below the surface of the synovial deposits, we identify an inhomogeneous distribution of the wear debris. This indicates the need to use multiple techniques in order to adequately identify the elemental composition of the prosthetic wear material. © 2007 Wiley Periodicals, Inc. J Biomed Mater Res 84A: 1068–1077, 2008

Key words: total knee arthroplasty; wear debris; XPS; EDS; Ti6Al4V; F-75 CoCrMo

INTRODUCTION

Total joint arthroplasty (TJA) has become a highly respected and successful treatment for patients suffering from arthritis. Despite its resounding clinical success, a small but significant number of these procedures still fall victim to failure. Frequently these failures are attributed to a detrimental biological response triggered by the generation of wear particles that dislodge from the prosthetic implant surfaces during normal activities.[1–3] As shown in Table I, the common materials of most modern-day prosthetic implants are titanium alloys (ASTM F-136, F-1108, and F-1472 Ti6%Al4%V), a cobalt–chromium alloy (ASTM F-75 CoCrMo), and ultrahigh molecular weight polyethylene (UHMWPE). When present in sufficient quantities, these prosthetic wear debris particles have been shown to stimulate a local biochemical cascade of events that often compromise the quality of bone adjacent to the implant.[4–6] This process, known as aseptic osteolysis, continues to be a major obstacle in the long-term performance of TJA.[7–13]

However, the literature appears quite confusing when addressing this bone resorptive phenomenon in relation to these various prosthetic alloys. While Ti6Al4V and F-75 CoCrMo are two of the most commonly used alloys in TJA, literature has shown their compositional elements of titanium (Ti), cobalt (Co), chromium (Cr), nickel (Ni), vanadium (V), manganese (Mn), and iron (Fe) to be some of the most biologically reactive elements that are capable of promoting both bone resorption and reduced bone proliferation.[2,6,14–17] While the debate over which implant alloys are the most suitable for extended implantation continues today, the question remains, is it the metallic debris in alloy form or the alloy's compositional element concentrations that are responsible for triggering this osteolytic process? Additionally, with a

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Contract grant sponsor: NIH-NIBIB; contract grant number: EB003397-01
Contract grant sponsors Summa Hospitals Foundation and Robertson-Hoyt

TABLE I
Composition Percentages of Prosthetic Alloys

	ASTM F-136, F-1108, and F-1472 Ti-6Al-4V	ASTM F-75 Co-Cr-Mo
Titanium (Ti)	88.5–92.0	–
Aluminum (Al)	5.5–6.75	–
Vanadium (V)	3.5–4.5	–
Iron (Fe)	0.25–0.30	0.75
Cobalt (Co)	–	57.4–65.0
Chromium (Cr)	–	27.0–30.0
Molybdenum (Mo)	–	5.0–7.0
Nickel (Ni)	–	2.5
Manganese (Mg)	–	1.0

resurgence in the usage of metal–metal articular joint resurfacing, a joint replacement system inherently more difficult to monitor surface wear by traditional methods (i.e., radiography), any ability to identify and measure prosthetic wear debris from small samples of aspirated joint fluid could have far reaching implications in monitoring patient sensitivity, aseptic osteolysis, and prosthetic wear rate.

While the industrial community already employs various surface analytical techniques to study such wear phenomena, as yet these methods have not been widely introduced into the biological community. Compositional techniques such as energy dispersive spectroscopy (EDS), micro-Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) are very sensitive tools capable of performing elemental measurements of bulk and fine material.

The purpose of this study is to determine whether the industrial spectroscopic methods of XPS, micro-Raman spectroscopy, or scanning electron microscopy (SEM) equipped with EDS can be used to identify compositional wearing of various metallic and nonmetallic prosthetic implant materials from aspirated joint fluid following total knee arthroplasty (TKA).

METHODS AND MATERIALS

Subjects

In this prospective study, four nonrheumatoid subjects scheduled to undergo revision TKA were voluntarily enrolled with signed informed consent (approved by the Institutional Review Boards of both institutions). The average age at the time of surgery was 78 ± 2 years with an 88 ± 29 month time to failure of the primary TKA (see Table II). While radiographs for all four subjects confirmed appropriate anatomical/mechanical placement of the components with no visual evidence of osteolysis, all four subjects were symptomatic to inflammatory-induced synovitis with prosthetic wear suspected as the cause.

Synovial aspiration

After the subject was brought to the operating room, anesthetized, prepped for their revision procedure, and under tourniquet control, an 18-gauge needle was inserted into the knee joint and the synovial fluid was aspirated. The extracted synovial fluid was immediately transferred into Vacutainer® tubes (Ryan Medical, Brentwood, TN) containing ethylenediaminetetraacetic acid (EDTA) and mixed thoroughly to prevent clotting. After mixing, the synovial fluid was transferred to 2 mL dolphin microcentrifuge tubes (Sorenson, West Salt Lake City, UT), numbered to conceal patient identities, and stored at −80°C. Table III categorizes each of the sample implant compositions and the extent of component wear as noted during intraoperative inspection.

Debris flake preparation and analyses

When the synovial specimens were needed for spectroscopic analysis, microcentrifuge tubes from each patient were brought to room temperature and centrifuged at $14{,}250 g_{av}$ for 7 min as previously described in our earlier work.[5] Following high-speed centrifugation, the supernatant (synovial fluid) was removed, leaving a small cup-shaped debris flake (measuring ≈ 4 mm × 4 mm) deposited at the base of each tube. Using a squirt bottle, each debris flake was carefully washed with 2 mL deionized water and decanted over four separate events, then thoroughly dried in preparation for spectroscopic analysis. Using fine-point 250 μL polypropylene pipette tips, each debris flake was carefully divided into two equal portions through its center apex, with one portion to be analyzed using SEM/EDS and its counterpart to be analyzed using XPS and micro-Raman.

Debris flake analyses by SEM/EDS were performed under low vacuum conditions with a JEOL instrument (model JSM-6480LV) using an electron gun operated at

TABLE II
Subject and Synovial Aspirate Information

Subject No.	006	014	016	017
Gender	Female	Male	Female	Male
Age (years)	81	78	78	76
Time to revision (months)	127	57	87	79
Synovial aspirate (mL)	22	8	16	16
Synovial aspirate color	Dark amber	Dark amber	Black	Black
Gross joint metalosis	No	No	Yes	Yes
Joint infection	None	None	None	None

TABLE III
Device Material and Intraoperative Wear Notations

Sample No.	Femoral Component	Tibial Base Plate	Metal-Backed Patella	Observed Wear
006	CoCrMo[a]	Ti6Al4V[b]	All Poly	Femoral burnishing/tibial-poly only/patella-poly only
014	CoCrMo[a]	Ti6Al4V[b]	All Poly	Femoral burnishing/tibial-poly only/patella-poly only
016	Ti6Al4V[c]	Ti6Al4V[d]	Ti6Al4V[d]	Femoral scoring/tibial-poly only/patella-poly & metal
017	Ti6Al4V[c]	Ti6Al4V[d]	Ti6Al4V[d]	Femoral scoring/tibial-poly only/patella-poly & metal

[a]F-75 CoCrMo.
[b]F-1472 Ti6Al4V.
[c]F-136 Ti6Al4V.
[d]F-1108 Ti6Al4V.

20 kV. For XPS analyses, each debris flake was mounted, in a convex-side-up geometry, to a load-lock sample holder, with care not to contaminate the specimen. The XPS analysis was performed in fixed analyzer transmission mode, under high vacuum conditions, using a spectrometer (model Kratos ES 300) equipped with an aluminum anode source operated at 12 kV. Ranging up to 7 h, argon ion sputtering (a below the surface penetration technique similar to ion milling used in electron microscopy) was performed on each XPS sample in order to remove surface contamination. Using ultra-high purity argon gas at a total pressure of 2×10^{-5} Torr, the sputtering rate was $\sim$0.63 nm/min. Using an ACTON InSpectrum CCD Spectrogram detector, micro-Raman spectroscopy was also performed on the samples to provide additional information about the metal oxides and the UHMWPE potentially present in each debris flake.

In addition to the synovial specimens, a commercially pure metal powder and two prosthetic metal powders, each containing an average particle size of 3 microns or less, were evenly placed onto separate mounting stubs using carbon tape and analyzed to serve as spectroscopic controls. The commercially pure metal powder, containing 99% titanium by metal basis, was purchased through Johnson Matthey (Ward Hill, MA). The prosthetic F-75 CoCrMo and Ti6Al4V alloy powders, contained by metal basis 65% Co, 28% Cr, 6% molybdenum (Mo) and 92% Ti, 6.75% Al, 4.5% V, respectively, were both procured through donations by Zimmer. (Warsaw, IN).

RESULTS

Subjects

Weight bearing and skyline films showed radiographic evidence of marginal joint space narrowing without metal-to-metal contact for subjects 006 and 014 and evidence of potential patellofemoral metal-to-metal engagement for subjects 016 and 017.

At the time of the revision surgeries, routine Gram stain and bacteriology culture techniques were performed on the synovial fluid and deep tissues to ensure the joints were free from infection. The subjects were also followed postoperatively for 1 year, at which time none showed signs of infection.

Using pulsating lavage and lap sponges, intraoperative inspection of the prostheses by the senior surgeon found all components to be well fixed but showed a wide range of gross visible wear. Subjects 006 and 014 showed signs of mild femoral burnishing of the condylar rails with mild and moderate evidence of polyethylene wear of the patellar and tibial components, respectively. During the tibial polyethylene insert exchange visual inspection found no evidence of tibial base plate wear or rim engagement. While no gross metalosis was seen in the joint tissues, a significant synovitis was notable for which a

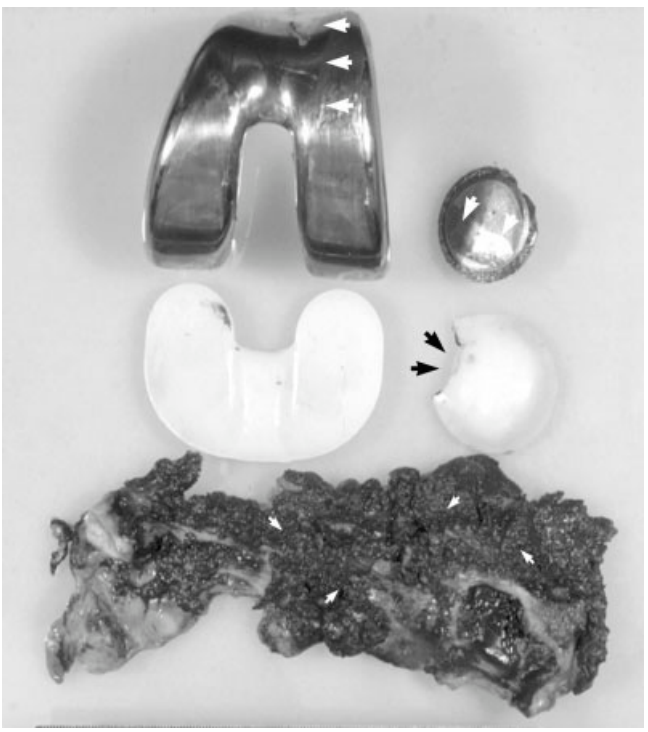


Figure 1. Retrieved Ti6Al4V components and synovial tissue. Note the femoral scoring, the localized polyethylene wear-through exposing a small lateral portion of the metal-backed patellar component (large arrows), and mild evidence of polyethylene wear of the tibial component. Also note the obvious metalosis apparent in the synovial tissue (small arrows), presumably blackened by oxidized Ti debris.

complete synovectomy was performed. Subjects 016 and 017 showed notable femoral scoring, localized polyethylene wear-through exposing a small lateral portion of the metal-backed patellar component, and mild evidence of polyethylene wear of the tibial component. An obvious metalosis was apparent in the joint tissues, presumably blackened by oxidized Ti debris, for which a tissue debridment followed by a complete synovectomy was performed (Fig. 1). The femoral and patellar components were replaced along with a tibial polyethylene insert exchange.

Synovial aspiration

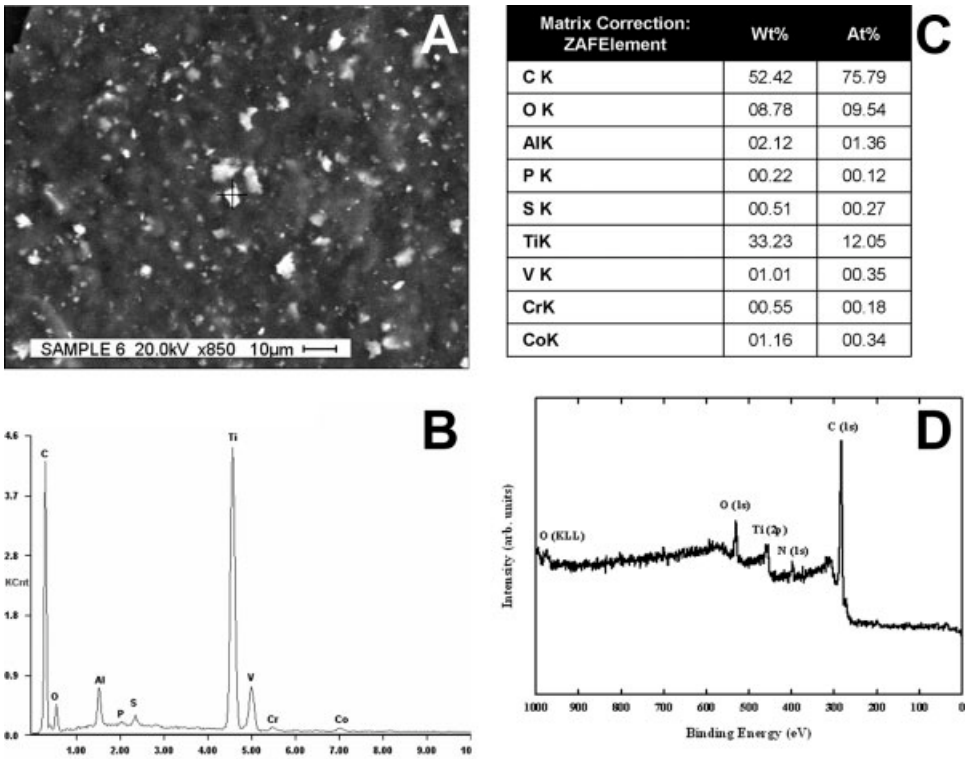
The average aspirate amount of synovial fluid was 16.0 ± 6.0 mL. All four fluid samples appeared less viscous in nature than that of ordinary joint fluid and ranged in color from black to dark amber. While gross metalosis was apparent in both samples collected from subjects implanted with components comprised exclusively of Ti6Al4V and a UHMWPE (samples 016 and 017), metalosis was not grossly apparent in the two samples collected from subjects implanted with a F-75 CoCrMo femur, a Ti6Al4V tibial plate, and an UHMWPE tibial insert and patellar components (samples 006 and 014). Results are summarized in Tables II and III.

Debris flake analyses

SEM/EDS

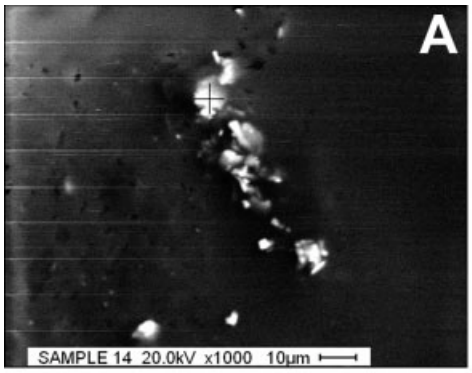
While several SEM/EDS area scans of sample 006 showed it to be predominately carbonaceous (C) by volume, the area scans also showed the sample to be highly populated with metal particulates. Shown in Figure 2(A) is a representative SEM area scan of a specific region of sample 006 that illustrates the numerous micron and sub-micron sized metallic-like debris particulates present in the sample. While repeated in other scans, the corresponding EDS spectrum of a single representative debris particle shows large amounts of Ti, moderate amounts of Al and V, and lesser amounts of Co and Cr present in the sample [Fig. 2(B)]. Interestingly, Figure 2(C) reveals that the Ti:Al:V weight percent ratio (Al-6.4%, V-3.0%) of the sample is very close to that of the originally manufactured product (Al-6%, V-4%).

Several SEM/EDS area scans of sample 014 also showed it to be comprised mainly of C with numer-



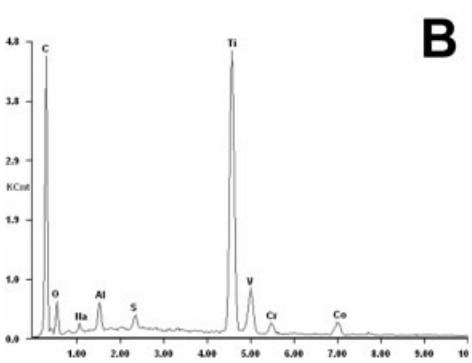
Matrix Correction: ZAFElement	Wt%	At%
C K	52.42	75.79
O K	08.78	09.54
AlK	02.12	01.36
P K	00.22	00.12
S K	00.51	00.27
TiK	33.23	12.05
V K	01.01	00.35
CrK	00.55	00.18
CoK	01.16	00.34

Figure 2. Spectroscopic analyses of the synovial debris flake from knee sample 006, a CoCrMo-Ti6Al4V device. A: An electron micrograph illustrating the abundance of micron and sub-micron metallic-like debris particles. B: An EDS scan of a representative particle [note the cross-hair, Fig. 2(A)], identifying Ti, Al, V, Co, and Cr debris. C: The corresponding EDS compositional breakdown of the particle. D: X-ray photoelectron area scan of the sample identifying the presence of Ti and O.



Matrix Correction: ZAFElement	Wt%	At%
C K	51.23	74.87
O K	09.18	10.07
NaK	00.76	00.58
AlK	01.52	00.99
S K	00.72	00.40
TiK	30.36	11.13
V K	00.91	00.31
CrK	01.62	00.55
CoK	03.69	01.10

C



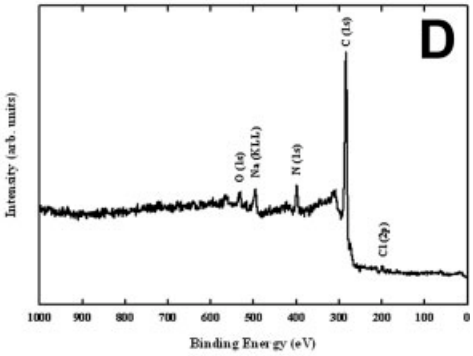


Figure 3. Spectroscopic analyses of the synovial debris flake from knee sample 014, a CoCrMo-Ti6Al4 device. A: An electron micrograph illustrating a small cluster of micron and sub-micron metallic-like debris particles. B: An EDS scan of a representative particle [note the cross-hair, Fig. 3(A)], identifying Ti, Al, V, Co, and Cr debris. C: The corresponding EDS compositional breakdown of the particle. D: A representative XPS area scan of the sample.

ous micron and sub-micron sized metallic-like debris particulates. Shown in Figure 3(A) is a representative SEM area scan of a specific region of sample 014 that illustrates a cluster of micron and sub-micron sized metallic-like debris particulates present in the sample. The corresponding EDS spectrum again shows roughly the same Ti:Al:V weight percent ratio (Al-5.0%, V-3.0%), with lesser amounts of Co and Cr present in the sample [Fig. 3(B,C)].

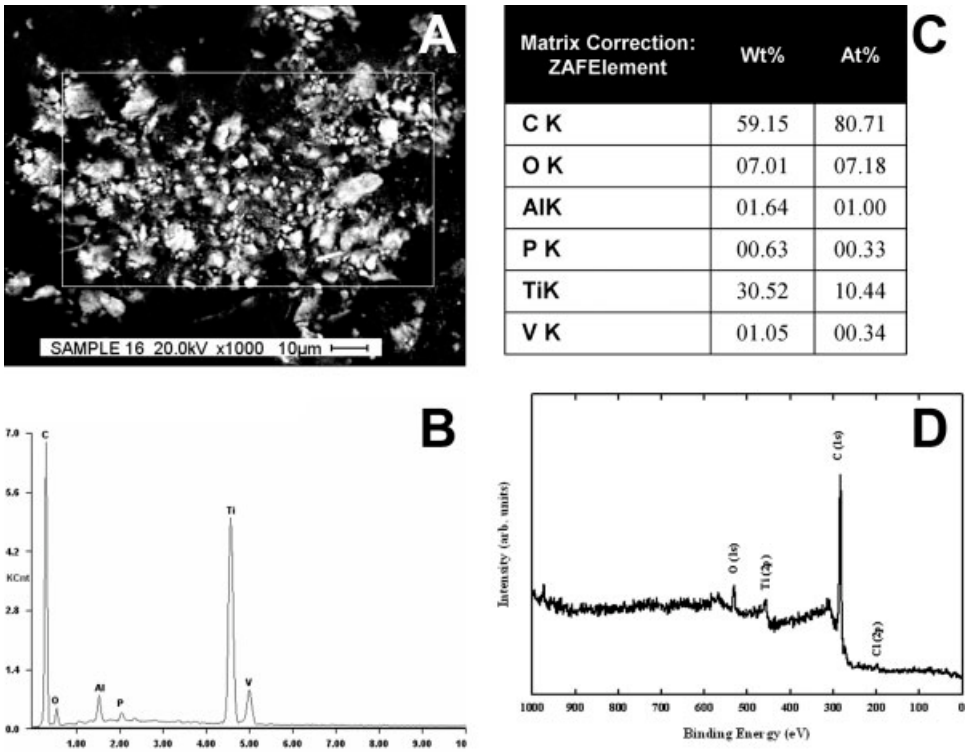
While several SEM/EDS area scans of sample 016 showed it to be predominately carbonaceous (C) by volume, the area scans again showed the sample to be highly populated with metal particulates. Shown in Figure 4(A,B) is a greater magnification of a representative clustering of micron and sub-micron sized metal-like particulates that are extensively comprised of Ti, Al, and V. This evidence corroborates well with the fact that the metal portion of the prosthetic implant used in this sample was comprised solely of Ti6Al4V material. Figure 4(C) shows the corresponding EDS material composition to be roughly the same Ti:Al:V weight percent ratio (Al-5.4%, V-3.4%) as the originally manufactured product.

While several SEM/EDS scans performed on multiple regions of sample 017 resulted in similar findings, Figure 5(A) illustrates a greater magnification SEM scan of a single sintered mass consisting of metallic particulates ranging from sub-micron to >10 microns in size that are comprised entirely of Ti, Al, and V [Fig. 5(B)], and have roughly the same Ti:Al:V weight ratio (Al-5.0%, V-3.0%) as the originally manufactured product [Fig. 5(C)].

XPS

Unlike EDS, XPS analysis was preceded by sputtering to remove surface contaminates and identifies the chemical compounds from the surface by probing vertically within the first few nanometers of each sample. To better illustrate this feature, Figure 6 shows a series of XPS survey scan spectra plotted versus sputtering time. Note how sputtering reveals the presence of oxygen (O) and Ti deep within the debris flake, indicating the sample to be vertically inhomogeneous.

After sputtering sample 006 for 5 h, the sample appeared predominately carbonaceous. However, Ti and O were detected, indicating the presence of oxidized Ti [Fig. 2(D)]. Interestingly, while the only available source of Ti wear in this sample would be from the Ti6Al4V tibial tray, no tibial tray wear was visually noted intraoperatively for this sample. This evidence, consistent with the EDS data [Fig. 2(B,C)],



Matrix Correction: ZAFElement	Wt%	At%
C K	59.15	80.71
O K	07.01	07.18
AlK	01.64	01.00
P K	00.63	00.33
TiK	30.52	10.44
V K	01.05	00.34

Figure 4. Spectroscopic analyses of the synovial debris flake from knee sample 016, an all Ti6Al4V device. A: An electron micrograph illustrating a single sintered mass consisting of metallic-like particulates. B: An EDS scan of the cluster [area within box, Fig. 4(A)], identifying large amounts of only Ti, Al, and V debris. C: The corresponding EDS compositional breakdown of the cluster. D: An XPS spectrum of the sample showing the presence of Ti and O.

appears to reflect backside wear in this sample that was otherwise nondetectable by radiograph or visual inspection.

After sputtering sample 014 for 7 h [Fig. 3(D)], the XPS scan again identified the material as predominately carbonaceous in nature, with some evidence of O, but unlike the EDS scan, failed to identify any metal wear debris.

After sample 016 was sputtered for 7 h, the XPS spectrum scan showed evidence of mainly C with moderate amounts of oxidized Ti present in the sample [Fig. 4(D)]. This evidence is consistent with both the EDS scan and the fact the prosthetic metal implant used in this sample was comprised solely of Ti6Al4V material.

The XPS spectrum scan of sample 017, following a 7 h sputtering process, again indicated the sample was primarily C with traces of Ti wear material [Fig. 5(D)]. This again is consistent with the fact that the material present is indicative of an all Ti6Al4V prosthetic implant.

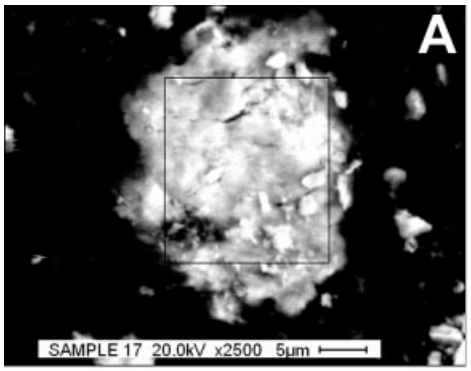
Multiple XPS spectra scans of the three control powders indicated the spectroscopic analysis to be accurate and reproducible. The XPS spectrum scan of the commercially pure titanium powder indicated the metal basis of the sample to be 96% pure [Fig. 7(A)]. The XPS spectrum scan of the prosthetic F-75 CoCrMo powder indicated the metal basis of the sample to be 68.7% Co, 28.2% Cr, and 3.2% Mo [Fig. 7(B)]. The XPS spectrum scan of the prosthetic Ti6Al4V powder indicated the metal basis of the sample to be 89.8% Ti, 10.3% Al, and 0.0% V [Fig. 7(C)].

Micro-Raman spectroscopy

A representative micro-Raman spectrum can be seen in Figure 8. While this technique failed to identify UHMWPE in any of the four samples, the scan did corroborate well with XPS data showing the presence of oxidized Ti wear debris present in the samples.

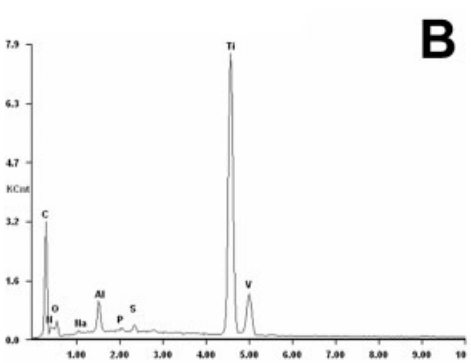
DISCUSSION

The long-term performance of joint replacement biomaterials is an area receiving significant attention in the orthopaedic community. Of particular concern is the generation of fine wear particulates by these modern-day prosthetic materials. Particulate wear debris in sufficient amounts has been shown to impede cellular and bone function at or near the bone-implant interface, leading to aseptic loosening and ultimately the failure of the artificial device.[5,18–22] Particularly important is the wear generation of fine metal debris



Matrix Correction: ZAFElement	Wt%	At%
C K	34.67	58.24
N K	05.98	08.61
O K	08.33	10.50
NaK	00.43	00.37
AlK	02.53	01.89
P K	00.27	00.18
S K	00.46	00.29
TiK	46.40	19.55
V K	00.95	00.37

C



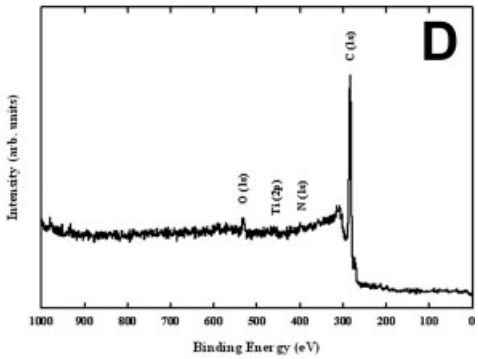


Figure 5. Spectroscopic analyses of the synovial debris flake from knee sample 017, an all Ti6Al4V device. A: A high magnification electron micrograph of a single sintered particle mass consisting of metallic-like particulates ranging from sub-micron to >10 microns in size. B: An EDS scan of the particle [area within box, Fig. 5(A)], identifying large amounts of Ti, Al, and V debris. C: The corresponding EDS compositional breakdown of the particle. D: An XPS spectrum of the sample showing the presence of Ti and O.

from the surfaces of the prosthesis. These common prosthetic metals have been shown to be quite toxic in the body, with the ability to alter normal bone homeostasis.[2,14,20–25]

According to preferential flow and effective joint space, the synovial fluid flows according to pressure gradients, following the path of least resistance and allowing particulate wear debris to be effectively transported throughout the entire joint space.[26] Because this flow of fluid and debris is bidirectional, the flow not only transports the wear particulates from the articular surfaces to remote periprosthetic spaces, but also transports the wear debris particulates back to the articular surfaces where it could potentially cause third-body wear. So while some wear debris may reside within the periprosthetic tissues, continuous amounts of wear particulates still reside within the joint fluid, making joint aspiration an effective and less invasive means to evaluate implant wear.

Using synovial joint aspirations, this work has introduced the industrial spectroscopic techniques of SEM/EDS, micro-Raman, and XPS to evaluate the composition of the particulate debris retrieved from the knee joint following knee replacement surgery. While our results indicate that these retrieved depos-

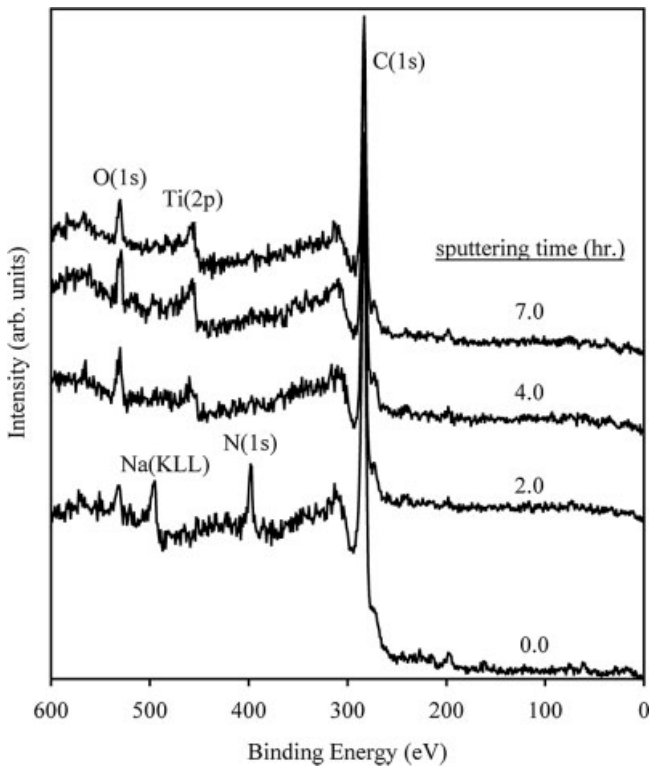


Figure 6. A series of XPS survey scan spectra plotted versus sputtering time of a single sample. Note the inhomogeneity as the sample is probed vertically below the surface.

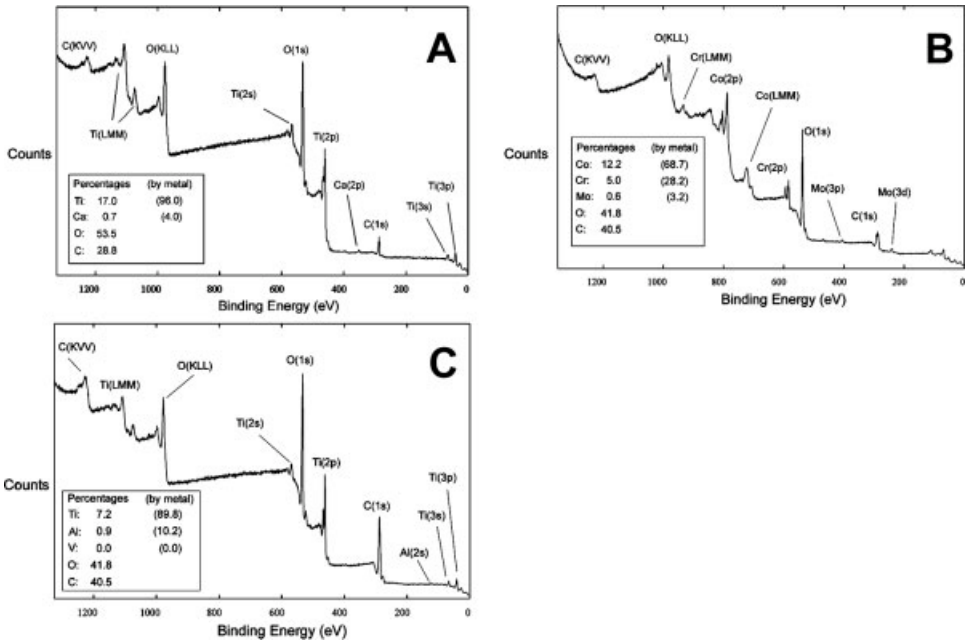


Figure 7. Representative XPS survey scan spectra of control powders. A: Confirmation of XPS to accurately identify the elemental composition of a commercially pure (99%) titanium powder. B: Confirmation of XPS to accurately identify the elemental composition of F-75 prosthetic 65%Co28%Cr6%Mo powder. C: Confirmation of XPS to accurately identify the elemental composition of prosthetic Ti6%AI4%V powder.

its are predominately carbonaceous by volume, these deposits also contain micron and submicron sized metallic particulates, some of which have been established to be the most biologically reactive (e.g., Co, Cr, Ti, Al).

Energy dispersive spectroscopy can be used to identify individual elements in bulk from large volumes of sample with an experimental uncertainty of 1–2%, assuming the sample is completely homogenous in the micron scale, and an experimental uncertainty less than 3% if the sample is not homogenous. In comparison, the more sensitive XPS analysis identifies chemical compounds from the surface of much smaller volumes of sample, probing vertically within the first few nanometers of the sample with an experimental uncertainty less than 5%. The vertical inhomogeneity of the samples as identified by XPS in this study compliments the EDS findings well, which indicate lateral inhomogeneity among our samples. Furthermore, XPS was successful in validating the elemental concentrations of a known commercially pure control metal powder and two prosthetic alloy powders.

As for the synovial samples, the fine metallic particles identified in this study appear to emanate from both the bearing (articulating) surfaces as well as from backside nonarticulating surfaces. The EDS spectrum scans for samples 006 and 014 show quantities of Co and Cr present, indicative of femoral articular surface wear. More interestingly, these two particular samples had Ti6Al4V tibial trays implanted that were not visually compromised. Yet both EDS and XPS spectra identified large amounts of Ti, Al, and V present within the debris flakes (Figs. 2 and 3). This backside wear data supports our previous XPS work using different samples with identical component wear configurations.[27]

While the EDS scans show a variety of metallic substances present in all samples, it may be questioned whether corrosive dissolution or actual wearing of the implant surfaces produced these elements. We

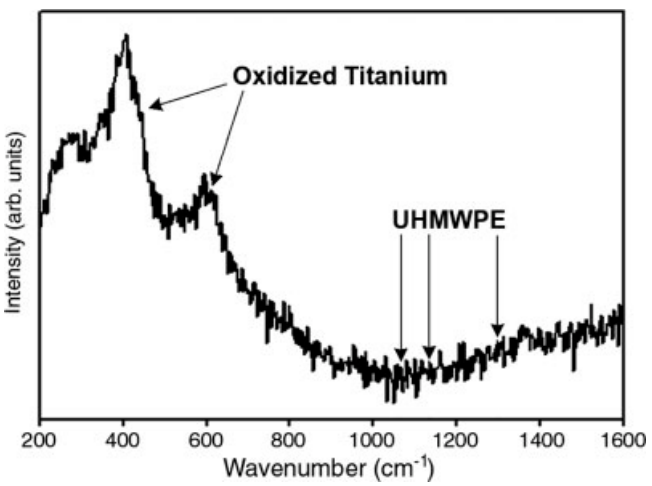


Figure 8. A typical micro-Raman spectrum scan of a synovial debris flake. Note the presence of titanium and oxygen, but the absence of any indicative features of ultrahigh molecular weight polyethylene.

point out that the Ti:Al:V ratios from EDS scans for all four samples are comparable to those of the original alloy composition. To further bolster these finding, our XPS results indicate that the samples with more titanium also contained the most oxygen. Since titanium wear particles would be expected to immediately react with oxygen available within the joint capsule to form a titanium oxide complex, and since both the XPS and micro-Raman scans indicate Ti and O present, we propose the materials are a result of prosthetic wear and not chemical dissolution of the implant surfaces.

Finally of concern in this study is the absence of Al, V, Co, Cr, Mo, and Ni in the XPS scans. However it is possible that the small sample size, less than optimal geometry (cup shape) and poor signal-to-noise ratio may have contributed to these null results. Thus, even though our XPS data detected large amounts of Ti from the Ti6Al4V complex, we may not necessarily have detected the Al and V present in much smaller quantities. More troubling though is the fact that UHMWPE was absent in the micro-Raman scans. Figure 8 illustrates a typical Raman spectrum where one would expect to see the indicative features that correspond to UHMWPE deposits. Our hypothesis is that the decanting of synovial fluid and multiple washings of the debris flakes with deionized water in preparation for spectroscopic analyses left only some sintered remnants of UHMWPE within the hard carbonaceous material and removed the majority of the lighter polyethylene particles from the samples prior to the testing. To further address this UHMWPE absence, our laboratories are evaluating other spectroscopic techniques that would permit analysis of the synovial fluid, for UHMWPE and metal particle debris, prior to centrifugation.

CONCLUSION

This study demonstrates a novel approach for introducing industrial spectroscopic techniques to identify fine metal wear particulates and other impurities deposited within the synovial fluid of postoperative TKA. More importantly, this study, using multiple spectroscopic techniques to probe both at and beneath the surface of synovial debris flakes, illustrates the inhomogeneous distribution of the wear debris and the need to use multiple techniques to identify the elemental composition of the material. While we were successful in identifying the key metallic materials produced by prosthetic wear, further investigations are warranted. With our recent acquisition of a more sensitive XPS system, coupled with other new spectroscopic tools now available to us, we plan to continue this research in hopes of establishing an early detection (prethreshold) means of identifying and monitoring *in vivo* total joint wear rates along with the deposition of unwarranted prosthetic metallic and nonmetallic particulates from small samples of aspirated joint fluid.

We also acknowledge the approvals to conduct this research by the Institutional Review Boards of both Summa Health System Hospitals and The University of Akron. We thank Jeanette Killius of the Northeastern Ohio Universities College of Medicine and Ruth Murray of Oxford Instruments, for their assistance with the SEM and EDS.

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