X-Ray Fluorescence Analysis of Sculpted Metal Alloys

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Analytical chemists are presented daily with a variety of real-world questions in which the chemical identification and quantification of a sample is the simplest part of the problem. In the past decade, the Internet has moved from the realm of computer science to all areas of life. The power of the Internet to augment traditional chemical analysis is beginning to be tapped to move the instrumental analysis course beyond simple chemical identification and quantification of ersatz samples to complete solution of problems. Complete solution of a problem is achieved when the analyst determines not just what an unknown sample is, but what it is used for and why. In contrast to analysis of the same laboratory mixtures year after year, complete solution of real problems intensifies student interest in laboratory experimentation, especially when a solution to a seemingly difficult problem is achieved in one afternoon. The result suggests that instrumental analysis laboratories should install Internet computers in the lab beside the usual instruments and teach Internet techniques along with instrumental theory and practice.

Introduction

One of the most interesting aspects of analytical chemistry research at a university is the diverse array of problems presented not by the usual federal agencies, but by others. These analytical problems can be used to stimulate undergraduate interest in chemical analysis. Periodically the state police bring forensic work. Occasionally insurance companies investigating fraud or seeking to identify stolen goods come with evidence. At other times, attorneys with product-tampering cases bring in samples. Occasionally, someone will even present evidence someone claims to have obtained from an extraterrestrial spacecraft. There is a nearly automatic bias against spending much time in the study of such samples. The perception always exists that these studies are a waste of time and resources, or worse, attract people with psychiatric problems or will simply result in an accumulation of hazardous waste in the lab. To avoid such problems, a prudent chemist examines only materials from cases previously screened by researchers connected with recognized organizations. Science demands some sort of mechanism for analyzing such samples, even if they are rare. After all, if scientists automatically dismissed every absurd idea without doing a single experiment, where would science be?

Psychologists or other professionals sometimes conduct interviews of “contactees” (people who claim or believe they have had contact with extraterrestrial technology or biological entities). This paper reports the results of the examination of two hard metal objects submitted by such a researcher. One object was left on each of two separate occasions by someone who claimed to be a contactee. Were the items really "souvenirs" picked up as proof of the visit while aboard a spacecraft? Or more likely, were the objects completely terrestrial in origin? These questions proved irresistible for the instrumental analysis students.

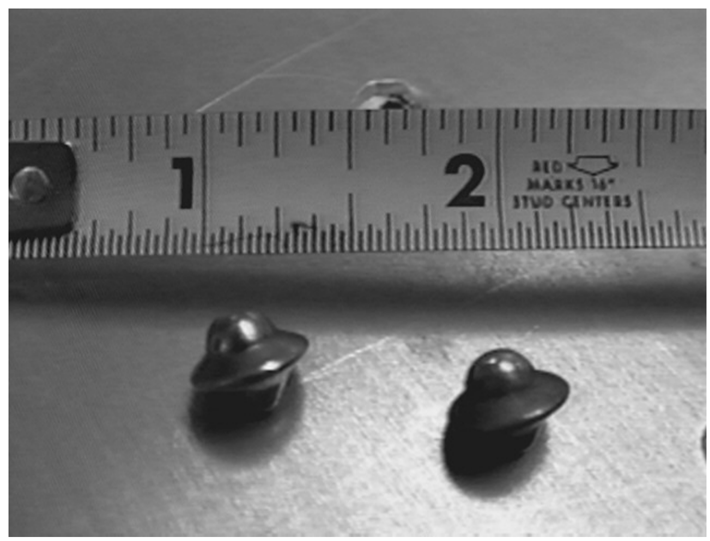


Figure 1. The metal sample on the right was brass plated.

The shape of the two objects was arguably similar to reported shapes of unidentified spacecraft (see Figure 1). The metal was polished, smooth and very hard (the objects could not be scratched by a metal file). The objects had a maximum diameter of 0.400 inch, and a maximum thickness of 0.320 inch. The hardness and shape suggested the objects were something comparable to tapered roller bearings. The objective of this exercise was to test the hypothesis that the objects were bearings by (1) searching for manufacturers of similar bearings, and (2) by experimentally determining whether the chemical composition of the objects was similar to that of commercially available bearings using scanning electron microscopy and x-ray fluorescence spectrometry.

X-ray fluorescence spectrometry (XRF) is a bulk characterization technique used for the rapid, simultaneous, and nondestructive detection of all elements heavier than fluorine[1]. In XRF the sample is irradiated with x-rays and re-emits x-rays with wavelengths that are characteristic of the sample composition. In contrast to fluorescence emission of visible light, which arises from valence (or outer) electronic shell transitions, x-ray fluorescence is x-ray photon emission by samples from inner shell electronic transitions. Thin layers of contamination, especially heavy metals, can often be detected with XRF. The advantages of using XRF spectrometry for samples include the fact that XRF is nondestructive, and provides quantitative analysis of bulk elemental composition as well as trace analysis (sensitivity) to parts-per-million (ppm) levels. Common applications of XRF include metal alloy analysis, detection of metallic contamination on and in plastics and polymers, and determination of pharmaceutical trace metals.

Experimental Section

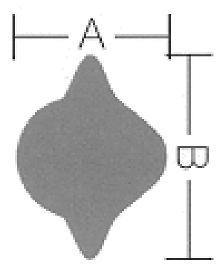
Instrumentation. A Hitachi 3200N variable-pressure scanning electron microscope with energy-dispersive x-ray spectroscopy (EDS) and 3.5 nm spatial resolution was used to collect spectra from the metal samples. The mass of the samples was determined using a top-loading balance. A Dell Pentium computer with Netscape was used for research on the Internet.

Internet Strategy. The search for similar bearings two took routes: (1) a search of the Internet for companies that manufacture a similar part, using both text and image searches, and (2) the posting of pictures of the objects to an Internet newsgroup (Usenet), where others could help to identify the objects.

A search engine, AltaVista[2], was used to seek manufacturers of bearings. AltaVista permits the results of searches for keywords and images to be refined by (1) performing a frequency analysis of other words on the pages with hits from a search for bearings, and (2), including or excluding pages with these new keywords from the frequency analysis in a Boolean fashion. An Internet newsgroup index service, DejaNews[3], was used to identify an appropriate news group on which to post photos of the objects. A search of the newsgroups for bearings using DejaNews suggested that a group called rec.crafts.metalworking would be very appropriate for posting the pictures, because many postings containing the word "bearings" or similar words were found in that newsgroup. However, no posting of binary files (including programs and pictures) is permitted on rec.crafts.metalworking. Binary files are posted on a web server at www.metalworking.com using an automated "drop box." Users of the newsgroup with binary files to post put the files in the drop box, and then post a message to the newsgroup giving the file name in the drop box. Other users of the newsgroup can then access both the text posting and the binary file. Analysts should check the FAQ (a Frequently Asked Questions list with answers) of each newsgroup for any special posting rules before making a post[4]. The FAQ or a pointer to it is usually posted to a newsgroup every week or two.

Results and Discussion

Using the Internet in this manner, it was determined that the objects were most likely 1/4 inch ballcones (see Figure 2). Ballcones are a tumbling medium used for burnishing metal parts and stones. Burnishing media like ballcones come in an assortment of shapes in order to reach into the recesses of work pieces. The AbbottBall Company in West Hartford, Connecticut is one manufacturer of ballcones that are apparently identical to the unknown objects[5].



size	Dimensions (inches) A	B
1/8"	.125	.170
5/32"	.215	.270
3/16"	.270	.300
1/4"	.320	.400
5/16"	.375	.465

Figure 2. The ballcone design combines the burnishing abilities of balls and cones into one carefully proportioned shape.

To confirm the identity of the parts as ballcones, several tests were performed.

1. The objects were determined to be ferromagnetic using a laboratory magnet.
2. The mean and standard deviation of the mass of each ballcone was measured (n=6 replicates). The unplated ballcone had a mass of 2.2640 g +/- 0.0010 g, while the brass-plated ballcone had a mass of 2.2702 g +/- .0013 g. The dimensions of the objects were measured as reported above.
3. Scanning electron microscopy was performed with x-ray fluorescence spectrometry to determine the elemental composition of the ballcones. The SEM images were unremarkable and were not retained. The parts were smooth except for microscopic oxygen- and carbon-containing "islands" that appeared similar to corrosion. X-ray fluorescence spectrometry was employed to identify the elements found in the objects. The chemical composition was compared with the composition of manufacturers of

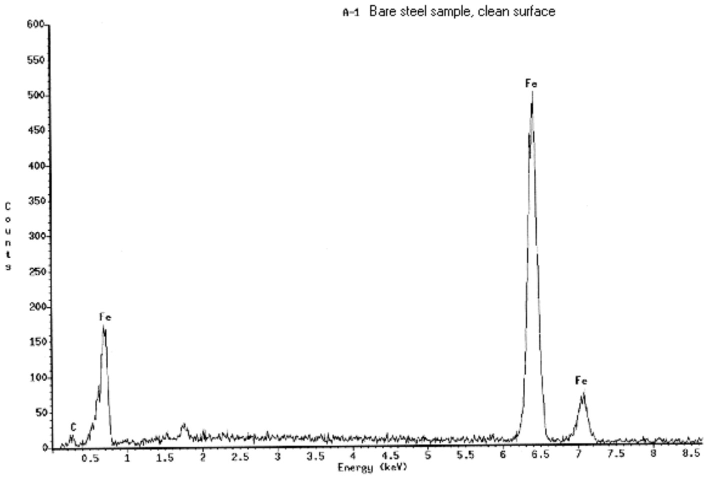


Figure 3a. X ray fluorescence spectrum of smooth metal of unplated ballcone.

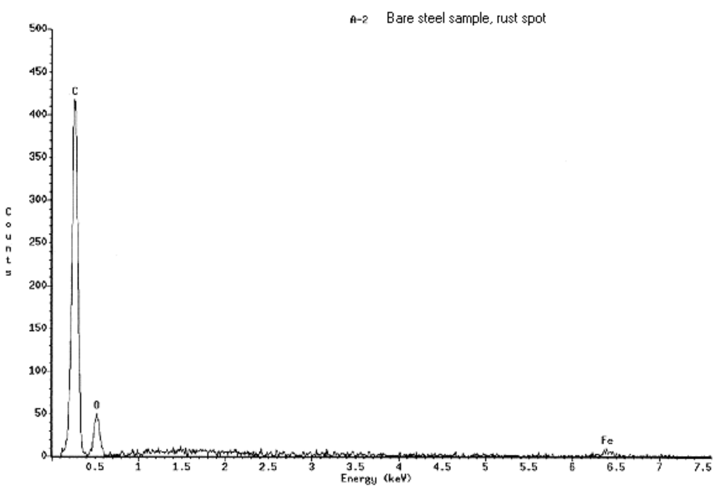


Figure 3b. X ray fluorescence spectrum of erosion spot of unplated ballcone.

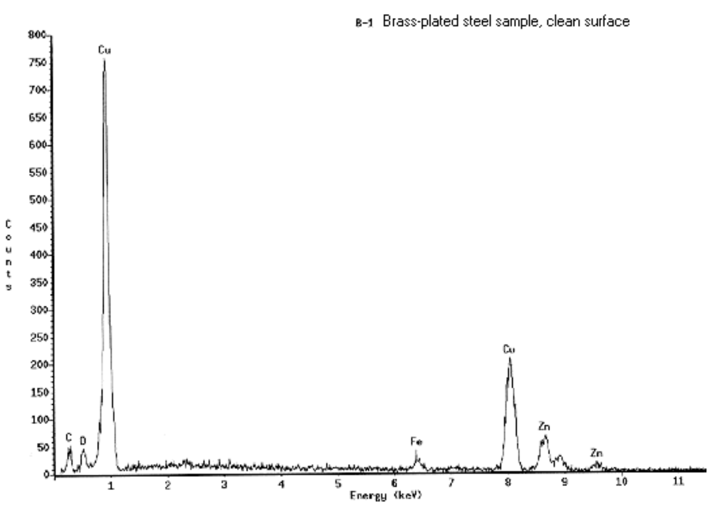


Figure 3c. X ray fluorescence spectrum of smooth metal of plated ballcone.

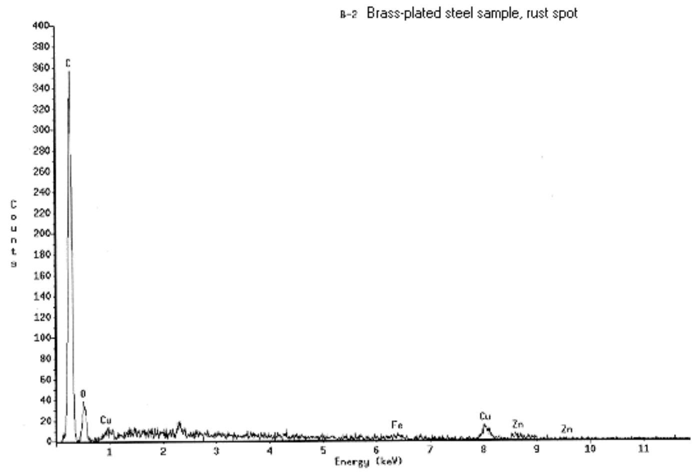


Figure 3d. X ray fluorescence spectrum of erosion spot of plated ballcone.

commercial ballcones to confirm identity. The shape matches (down to the exact dimensions of 1/4-inch ballcones) those of at least one commercial manufacturer, AbbottBall Company in West Hartford, Connecticut. Figure 3 shows the x-ray spectra of the plated and unplated ballcone and the oxygen- and carbon-containing areas on each ballcone. The elemental analysis results are similar to the composition of commercial ballcones made by AbbottBall. Carbon steel contains small amounts of carbon, as well as manganese, phosphorous, and sulfur. The brass plating is a mixture of copper and zinc. Detailed specifications of AbbottBall's various products are given on the company web site[4].

Conclusion

While the identification of the items as burnishing media with a terrestrial use does not logically rule out the possibility that spacecraft could include polishing equipment, the Law of Parsimony suggests that the ballcones came from a terrestrial shop. This conclusion leaves the psychologists and physicians to discover why the ballcones were represented in the way that they were. More important, the episode reveals the power the Internet provides analytical chemists in reaching a solution to a seemingly tedious problem (identifying the actual use of an unknown object) in one afternoon. Instrumental analysis laboratories might do well to install Internet computers in the lab alongside the HPLC, FTIR and NMR, and teach image searching, the Usenet, drop boxes and "netiquette" along with instrumental theory and practice. This in turn will enable more interesting laboratory exercises, and provide an impressive demonstration of chemical analysis for undergraduates.

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