Analyses of Bronzes

Application Note

Atomic Absorption

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Introduction

Late in 1981 a technical investigation of the approximately 3000 year old bronze objects in the Eli Lilly Collection of Chinese Art was begun. Encouraged by the Indianapolis Museum of Art's Curator of Oriental Art, Dr. Yutake Mino, the analytical procedure was outlined and carried out by Dr. Leon Stodulski, Ms. Portia Bass, and Ms. Mary F. Striegel of the Analytical Chemistry Division of Indiana University–Purdue University at Indianapolis. Dr. James Robinson, Assistant Curator of Oriental Art and Mr. Richard Sherin, Conservator of Objects, were the museum collaborators during the course of this study.

A co-operative effort was necessary between materials analyst, curator, and conservator to obtain, assimilate, and apply the curatorial and art historical information currently available and the newly generated materials analysis data. The cooperation between the IMA staff, the Analytical Chemistry Division of I.U.P.U.I., and several high-technology industrial organizations has resulted in the important, in-depth look at the very valuable Lilly Collection of Chinese Bronzes reported here.

In the past, x-radiography has proved to be a very useful tool in the technical examination of ancient bronze vessels. It reveals much information about their true, (present) condition, and often provides clues concerning the fabrication techniques used by ancient artisans. The first task then was to x-radiograph each of the bronzes, the resulting x-radiographs allowing us to make a precise determination of appropriate and representative sites from which to extract samples for the next step in the study, the analyses of the alloys. These analyses were accomplished using Atomic Emission Spectrography and Atomic Absorption Spectrophotometery. It was determined in preliminary experiments that the analyses could be accomplished with only 15 milligrams of alloy. Using the x-radiographs as a guide, an obscure but apparently representative site on each vessel from which to extract the sample was selected. Samples were removed with a small (No. 60) steel drill bit. The purity of each sample taken for analysis was determined by observing the removed material under a polarizing microscope and estimating the amounts of copper and other metal reaction products present. Once a sufficiently clean sample was collected from each site, the small hole created was immediately and completely filled with pigmented microcrystalline wax to match the surrounding color of the corrosion products or patina on the surface of the vessel. Sample sites on each vessel were documented both in writing and in photographs for future reference.

Features Revealed by X-Radiographs

X-radiographs readily indicate the existence and extent of cracks and other casting flaws created within the object by unequal stresses during improper cooling of the molten alloy in the mold. For example, in the vessel shown in Figure 1, a 12th–11th century B.C. Shang dynasty jia, or ceremonial libation vessel (IMA #60.33), the presence of a significant number of "blowholes" (indicating porosity of the alloy) – seen as small black spots – is clearly illustrated. These blowholes result from evolved gases trapped within the material after the molten alloy was poured into the mold. As a result, small voids were created in the cast form when these gases, upon cooling, gradually diffused out through the metal. A knowledge of the location and concentration of these voids can indicate relatively weaker areas of a vessel, and likelier sites for possible accelerated corrosion.

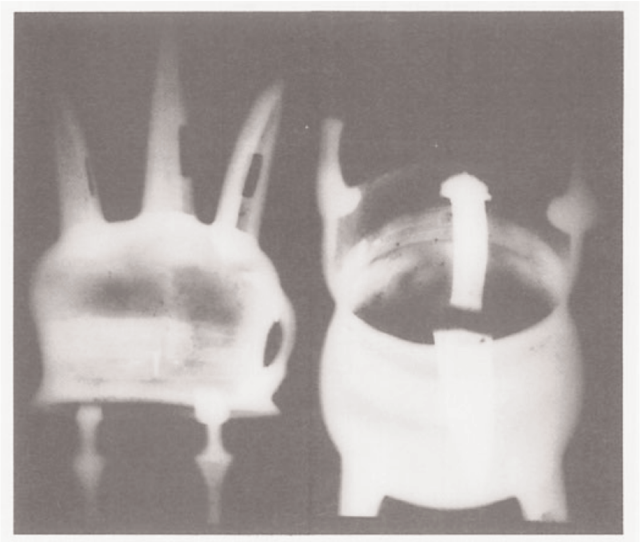

Figure 1. X-radiograph (2 views) of 12th-11th century B.C. Shang dynasty jia (IMA# 60.33) showing voids in alloy.

Often, more often than one might expect, missing parts and sometimes entire sections have been extensively "restored" at some point in the vessel's history. Such "restorations" were most often made with lead, lead-tin solder, copper metal, plaster of Paris, or some other material. Usually they are cleverly disguised by the application of a falsified patina of some kind, making it very difficult if not impossible for the naked eye alone to determine even their existence, much less their extent. Such repairs often do not hold together well, because these repair materials do not adhere well to old, corroded metal.

An example of an extensively repaired vessel is the 10th Century BC Western Zhou dynasty you, or ceremonial swing-handled wine container (IMA #60.24) shown in Figure 2. Here, the actual condition of this vessel was a surprise since all repairs had been cleverly hidden beneath a falsified patina. The many broken pieces have been remarkably well reassembled with (in all probability) a lead-tin solder. All broken pieces appear to be original to this one vessel, as judged by their similar densities in the x-radiograph. Small, hair-line cracks can also be seen.

The art of soldering is an ancient process. It therefore is difficult, if possible at all, to determine whether a repair is a "new" one or an "ancient" one. Lead-tin solders vary in their percent composition, with a 2:1, Sn:Pb combination (63% Sn:37% Pb) having the lowest melting point of all possible combinations of these two metals. It is also the "hardest" of all the lead-tin soft solders. It therefore possesses the two properties most desirable in a soft solder (used for repair purposes): a low melting point (183% °C), and strength. (N.B. A soft solder of 46% Sn:54% Pb + ¼-½% antimony added is the strongest form of soft solder.)

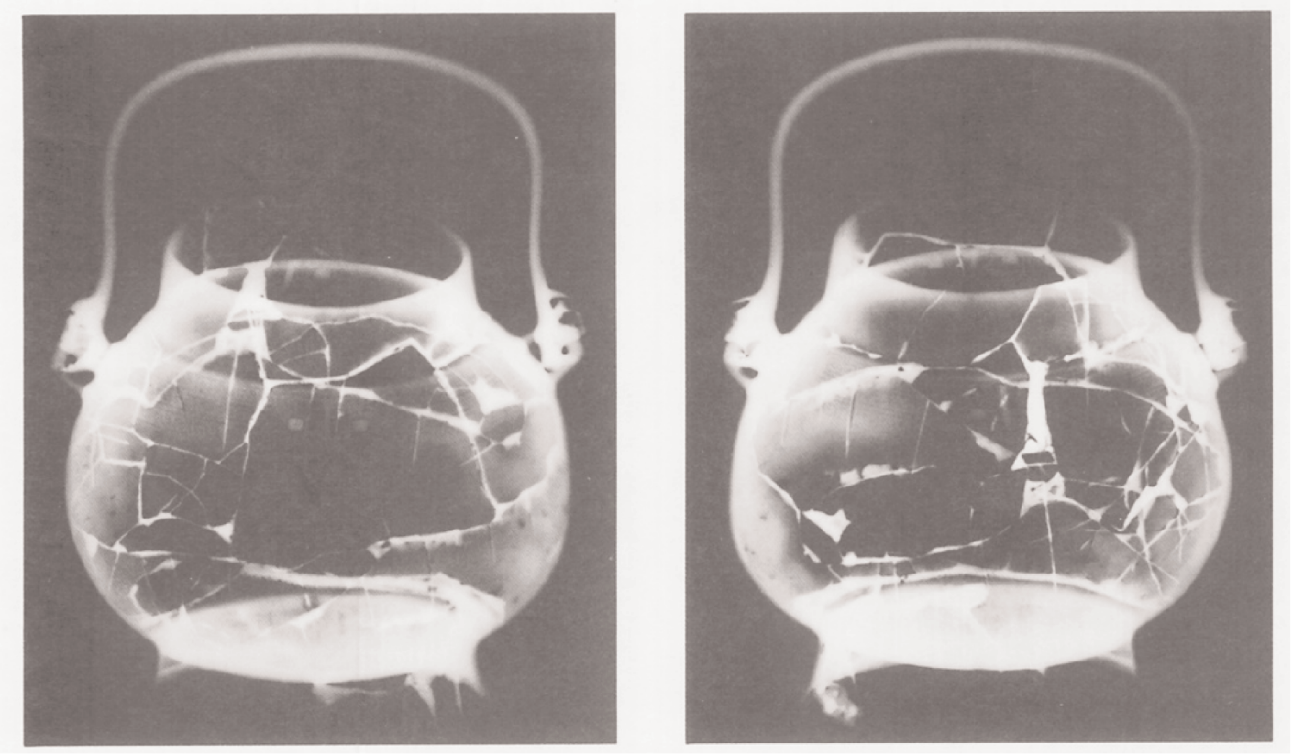

Figure 2. X-radiograph (front and back views) of 10th century B.C. Western Zhou dynasty you (IMA# 60.24) showing extensive repair and high density repair material, presumably Sn:Pb solder.

The lid to this vessel (Figure 3) had been suspected of being a complete forgery. This conclusion, to the time of this study, had been entirely based on a visual examination of its surface and decor. The radiograph immediately indicates a substantial difference between the character of the metal of the lid or cover and that of the alloy of the vessel body – the material of the cover, both perimeter and top, is much more uniform and homogeneous. A join can even be readily seen in the perimeter which may indicate, because of a lack of significant density, a forge-welded join. This then would further suggest that perhaps the cover had not been cast at all, but rather had been fashioned (at a much later time) out of sheet copper. The elemental analyses of a sample taken from the edge of the perimeter corroborated this observation by showing that it consists of approximately 96% copper, but very little tin, lead or zinc.

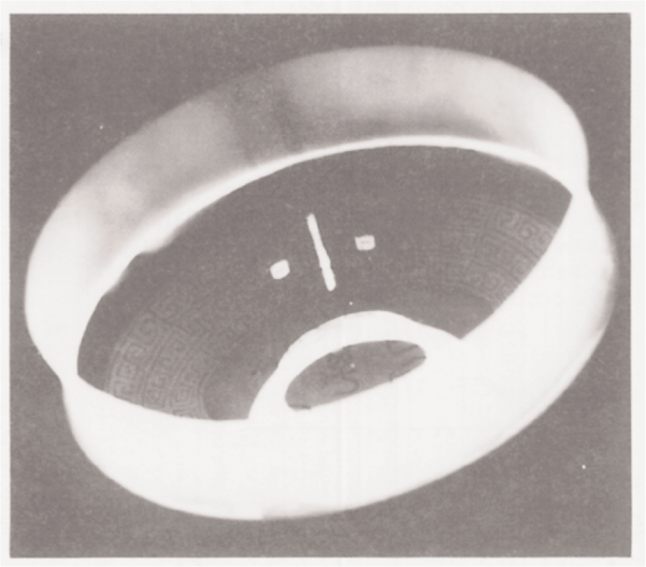

Figure 3. X-radiograph of cover of 10th century B.C. you (shown in Figure 2) showing probably modern join in perimeter.

Analyses Goals

Prior to this study, the Lilly Oriental Bronzes had not been sampled or subjected to any modern materials analysis techniques. It was therefore our purpose to quantitatively determine, as accurately as possible, the concentrations of those metallic elements most likely to be of archaeological and art historical significance to the other scholars. Furthermore, we proposed to accomplish this with the expenditure of as little of the valuable sample material as was practical. The instrumental techniques chosen for these analyses were the mutually complementary ones of Atomic Emission Spectrography (AES) and Atomic Absorption Spectroscopy (AAS). AES is especially suitable for analyses of materials that contain a large number of different elements in major, minor and trace concentrations. It also has the advantage of enabling the analyst to qualitatively and quantitatively determine these elements simultaneously from the consumption of a single, very small sample. AAS requires that certain specialized pieces of equipment be used for the analysis of each element of interest, which means that these elements must be determined sequentially, rather than simultaneously (as with the AES technique). This usually demands the expenditure of more sample material than is needed for AES analysis, a disadvantage that is more than compensated for by the fact that AAS analyses provide results of greater accuracy for elements present in major, minor and trace amounts than is usually possible by the AES technique. Also, by careful refinement of this method, and by using the sensitive instrumentation available to-day, such as the Agilent AA-875, the analyst can provide very accurate results from an adequately small sample.

The ultimate goal of such an analysis in the present study was to provide an elemental "fingerprint" of an unknown material, of sufficient scope and accuracy, that it can be used to clearly characterize that material. It is of prime importance to know exactly how much reliance can be placed on the analytical data generated, so that one is able to state with confidence that a particular difference between the compositions of two samples is, or is not, truly significant – and not due to the experimental uncertainty inherent in the analytical method employed. The present study reports the determination of copper, tin, lead, zinc, arsenic, nickel, iron, manganese, silicon, phosphorus, antimony and aluminium by AES analyses, and of copper, tin, lead and zinc by AAS.

Finally, the information obtained from these studies, and its art historical/curatorial significance, is discussed.

Description of Analytical Methods

Atomic Emission Spectrographic Analyses

The instrument used in this phase of the study was an Applied Research Laboratories Spectrographic Analyzer, using dc arc sample excitation photographic film detection.

The development of the quantitative AES method for the analyses of the Lilly alloy samples required the use of a series of twelve different National Bureau of Standards (NBS) and British Chemical Standards (BCS) bronze and brass alloys which contained accurately known amounts of the twelve different elements mentioned above. A sample of 99.999% pure copper metal was also used. A 5.0 ± 0.1 milligram portion of each standard alloy was weighed on an analytical balance, thoroughly mixed with an equal weight of a 90% (by weight) pure graphite powder/10% (by weight) germanium dioxide mixture (to eliminate loss of sample during heating), placed in a graphite sample electrode, and completely vaporized by the electric arc of the Spectrograph over a period of two minutes.

Multiple samples of each standard alloy were vaporized. The intensities of previously selected emission lines (or analytical lines), one from the spectrum of each of the twelve elements to be determined – were measured from the films produced as a result of the excitation and consumption of each standard sample. The intensity values obtained for each analytical line were averaged, and plotted against the known percent concentration of the respective element contained in the standard. A computer was used to produce this curve. The computer was programmed to also provide the equation of the curve which best fit all the experimental data points plotted. Calibration curves for each of the twelve elements were thus obtained. The one for copper is shown in Figure 4.

The reliability of the AES analytical method was determined in the following manner. Three of the available standard alloys were re-analyzed as if they were unknown materials, and the percentage of each element calculated from the appropriate calibration curve equation. Three "composite alloys" were also produced by mixing together exactly 2.50 ± 0.01 milligrams each of two different standard alloys, and similarly analyzed. Duplicate determinations of each of these standard materials were performed. Comparisons of experimentally calculated percent compositional values with known (true) values provided a measure of method accuracy. The difference between duplicate analyses of the same standard material gave an estimate of the reproducibility of the analytical method. The experimental uncertainty of the AES technique was obtained by calculating the percentage difference between the experimental and known values, and averaging these individual positive and negative deviations from the known value, without regard to sign, to obtain an "average % relative absolute error" for each amount determined. Average errors varied from ± 10% (of the value calculated) for copper to ± 50% for silicon – an element present in quite low concentrations, and therefore very difficult to determine accurately. Average errors for most of the other elements were in the region of ± 15% to ± 20%.

It was known from the beginning of this study that sufficient sample for duplicate analyses of some of the Lilly Bronze alloys might not be made available, and that the results of single determinations would have to be relied upon to provide the elemental "fingerprint" desired. Inspection of the results of individual alloy composition determinations in Table 1, and comparison of them with both average experimental and known values, reveals that they do provide a good estimate of alloy composition.

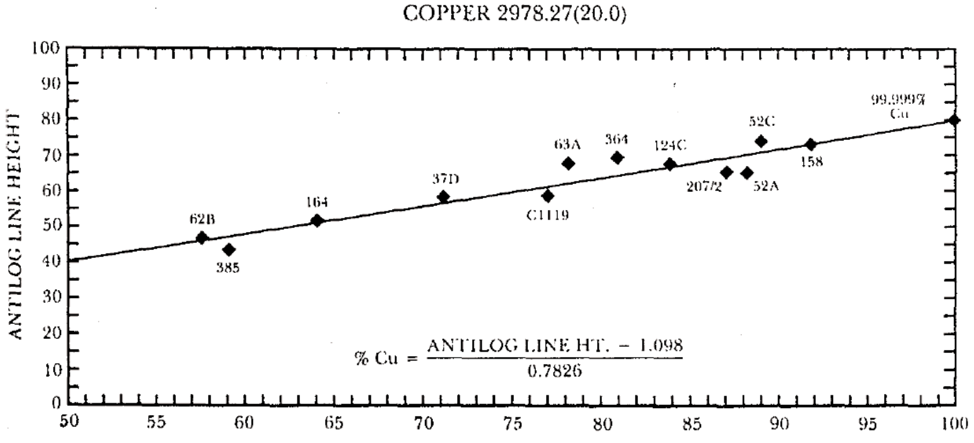

Figure 4. Calibration curve for Cu 2978.27A° line in the range of 55–100%. NBS and BCS standard alloys, and pure copper metal, are indicated.

Furthermore, the experimental uncertainty of each value determined provides a realistic estimate of the reliability of that value. Attention is drawn to the fact that the copper content of these alloys was determined by two different procedures – by measurement of the copper analytical line intensity, as described above, and also by difference; that is, by adding together the percentages of all the minor and trace elements present, and subtracting this value from 100%. The results of both methods are shown in Table 1. In the case of four of the six standards analyzed it is obvious that the difference procedure provides the accurate value.

The actual analyses of the Lilly Bronze alloys followed the procedure outlined for the standard alloy analyses.

Table 1. Atomic Emission Spectrographic Analyses of Standard Alloys

NBS 124C

	Percent Element Calculated			Percent known
Element	**Trial 1**	**Trial 2**	**Average**	
Cu	81.2 ± 8.1	81.2 ± 8.1	81.2 ± 8.1	84.22
Cu*	84.1	86.3	85.2	
Sn	5.39 ± 0.54	4.88 ± 0.49	5.14 ± 0.51	5.13
Pb	4.53 ± 0.68	3.86 ± 0.58	4.20 ± 0.63	4.74
Zn	4.79 ± 0.72	3.89 ± 0.58	4.34 ± 0.65	4.93
As	< 0.015	< 0.015	< 0.015	~ 0.002
Fe	0.192 ± 0.096	0.186 ± 0.093	0.189 ± 0.095	0.107
Ni	0.67 ± 0.13	0.63 ± 0.13	0.65 ± 0.13	0.60
Sb	0.32 ± 0.13	0.22 ± 0.008	0.27 ± 0.11	0.20
Al	< 0.50	< 0.50	< 0.50	–
Si	< 0.005	< 0.005	< 0.005	0.002
P	< 0.05	< 0.05	< 0.05	0.024
Mn	< 0.10	< 0.10	< 0.10	–

BCS 207/2

	Percent Element Calculated			Percent known
Element	**Trial 1**	**Trial 2**	**Average**	
Cu	83.1 ± 8.3	79.3 ± 7.9	81.2 ± 8.1	87.3
Cu*	87.1	88.9	88.0	
Sn	9.82 ± 1.5	8.56 ± 1.3	9.19 ± 1.4	9.74
Pb	≤ 1.0 > 0.15	≤ 1.0 > 0.15	< 1.0 > 0.15	0.70
Zn	2.12 ± 0.32	1.68 ± 0.25	1.90 ± 0.29	1.60
As	0.077 ± 0.019	0.10 ± 0.025	0.09 ± 0.022	0.066
Fe	0.054 ± 0.027	0.06 ± 0.034	0.061 ± 0.031	0.029
Ni	0.45 ± 0.090	0.37 ± 0.074	0.41 ± 0.082	0.29
Sb	0.16 ± 0.064	0.13 ± 0.052	0.14 ± 0.056	0.10
Al	< 0.50	< 0.50	< 0.50	0.014
Si	≥ 0.015	≥ 0.015	≥ 0.015	0.016
P	< 0.05	< 0.05	< 0.05	0.018
Mn	< 0.10	< 0.10	< 0.10	–

NBS 37D

	Percent Element Calculated			Percent known
Element	**Trial 1**	**Trial 2**	**Average**	
Cu	81.2 ± 8.1	79.3 ± 7.9	80.3 ± 8.0	70.78
Cu*	< 88.6	< 89.5	< 89.0	
Sn	1.58 ± 0.32	0.92 ± 0.18	1.25 ± 0.25	0.97
Pb	≤ 1.0 > 0.15	≤ 1.0 > 0.15	≤1.0 > 0.15	0.94
Zn	> 8.0	> 8.0	> 8.0	26.65
As	< 0.015	< 0.015	< 0.015	–
Fe	0.17 ± 0.076	0.13 ± 0.065	0.152 ± 0.076	0.76
Ni	0.63 ± 0.13	0.46 ± 0.092	0.55 ± 0.11	0.58
Sb	< 0.10	< 0.10	< 0.10	–
Al	< 0.50	< 0.50	< 0.50	–
Si	< 0.005	< 0.005	< 0.005	–
P	< 0.05	< 0.05	< 0.05	–
Mn	< 0.10	< 0.10	< 0.10	–

* Copper by difference.

Table 1. Atomic Emission Spectrographic Analyses of Standard Alloys (continued)

NBS 158/NBS 63A

	Percent element calculated			Percent
Element	**Trial 1**	**Trial 2**	**Average**	**known**
Cu	72.3 ± 7.2	91.1 ± 9.1	81.7 ± 8.2	84.67
Cu*	85.9	86.3	86.2	
Sn	5.57 ± 0.56	5.57 ± 0.56	5.51 ± 0.56	5.37
Pb	4.53 ± 0.68	4.19 ± 0.63	4.36 ± 0.65	4.46
Zn	1.68 ± 0.25	1.21 ± 0.18	1.45 ± 0.21	1.34
As	< 0.015	< 0.015	< 0.015	0.014
Fe	0.71 ± 0.18	0.79 ± 0.20	0.75 ± 0.19	1.0
Ni	0.21 ± 0.042	0.21 ± 0.042	0.21 ± 0.042	0.16
Sb	0.28 ± 0.11	0.27 ± 0.11	0.28 ± 0.11	0.25
Al	< 0.50	< 0.50	< 0.50	0.27
Si	> > 0.015	> > 0.015	> > 0.015	1.36
P	0.47	0.41	0.44	0.29
Mn	0.59	0.86	0.73	0.66

NBS 158/NBS 63A

	Percent element calculated			Percent
Element	**Trial 1**	**Trial 2**	**Average**	**known**
Cu	79.3 ± 7.9	77.6 ± 7.8	78.5 ± 7.9	70.81
Cu*	< 85.6	< 85.2	< 85.4	
Sn	2.28 ± 0.46	2.67 ± 0.27	2.48 ± 0.50	3.05
Pb	2.52 ± 0.38	2.46 ± 0.37	2.49 ± 0.37	2.51
Zn	> 8.0	> 8.0	> 8.0	21.45
As	< 0.015	< 0.015	< 0.015	~0.003
Fe	0.51 ± 0.077	0.48 ± 0.072	0.50 ± 0.075	0.464
Ni	0.36 ± 0.072	0.51 ± 0.10	0.44 ± 0.088	0.435
Sb	0.22 ± 0.088	0.14 ± 0.056	0.18 ± 0.072	0.103
Al	≤ 0.05	≤ 0.50	≤ 0.50	0.49
Si	0.014 ± 0.007	0.015 ± 0.008	0.015 ± 0.008	0.025
P	< 0.50	< 0.50	< 0.50	0.012
Mn	0.50 ± 0.10	0.56 ± 0.11	0.53 ± 0.11	0.65

NBS 158/NBS 63A

	Percent element calculated			Percent
Element	**Trial 1**	**Trial 2**	**Average**	**known**
Cu	79.3 ± 7.9	79.3 ± 7.9	79.3 ± 7.9	87.74
Cu*	88.0	86.6	87.3	
Sn	8.17 ± 1.2	10.2 ± 1.5	9.19 ± 1.4	8.79
Pb	< 1.0 > 0.15	< 1.0 > 0.15	< 1.0 > 0.15	0.36
Zn	3.02 ± 0.45	2.38 ± 0.36	2.70 ± 0.41	2.39
As	0.028 ± 0.007	0.027 ± 0.007	0.028 ± 0.007	0.035
Fe	0.064 ± 0.032	0.057 ± 0.029	0.61 ± 0.030	0.040
Ni	0.48 ± 0.096	0.54 ± 0.11	0.51 ± 0.100	0.51
Sb	≤ 0.10	≤ 0.10	≤ 0.10	0.052
Al	< 0.50	< 0.50	< 0.50	0.007
Si	0.012 ± 0.006	0.015 ± 0.008	0.014 ± 0.007	0.0085
P	< 0.05	< 0.05	< 0.05	0.0095
Mn	< 0.10	< 0.10	< 0.10	0.01

* Copper by difference.

A 5.0 milligram portion of each sample was weighed, mixed with 90% graphite/10% germanium dioxide, placed in a graphite electrode, and vaporized in the Spectrograph for two minutes. Great care was taken to ensure that all conditions for the analysis of the unknown materials were exactly the same as those for the standard alloys. The intensities of the analytical lines of the twelve elements of interest were measured from the spectrographic films, and the percent concentration of each element calculated from the appropriate calibration curve equation. The results of these analyses are presented in Table 3, along with the atomic absorption analytical data, and are discussed in later sections.

Atomic Absorption Spectrophotometric Analyses

These analyses were accomplished by flame AAS using an Agilent AA-875 atomic absorption spectrophotometer.

The determination of Cu, Sn, Pb, and Zn in the present study required the use of four individual hollow cathode lamps. It was necessary to develop a separate set of instrumental conditions for the determination of each of these four metals. Conditions such as flame stoichiometry, sample aspiration rate, the portion of the flame through which the radiation beam passes, and radiation intensity from the lamp all had to be optimized for each element in order to provide maximum instrumental sensitivity, thereby reducing the amount of sample required to obtain accurate analytical results. Some of the conditions required for the analysis of tin are illustrative of the precautions that were necessary in these studies. It was discovered that tin-containing alloys dissolved completely in acid solution but that tin exhibited the tendency to precipitate out of solution after a few days. Therefore, solutions containing tin had to be measured within 24 hours of sample dissolution. The determination of tin also required a hotter nitrous oxide-acetylene flame, whereas the other three elements were better handled using a cooler air-acetylene flame. Finally, it was found that the presence of large amounts of copper gave falsely-high tin absorbances. This effect was compensated for by adding known amounts of copper to the standard tin solutions used to determine the tin content of the Lilly Bronze alloys.

Quantitative AAS determinations required the establishment and use of a separate calibration curve for each metal. Standard solutions of each of these metals were prepared from 99.999% pure copper, tin, lead and zinc, weighed to an accuracy of at least ± 0.1% on an analytical balance, dissolved in a small amount of 3 parts concentrated hyrochloric acid/1 part concentrated nitric acid mixture, and diluted with distilled water to known volumes. Each of these metal solutions was further diluted to produce a series of standard solutions, of known concentration, for each metal. Each series of standard solutions was then used to provide the respective calibration curve. All volumetric glassware used was specially calibrated to within ± 0.1%. A computer was used to plot absorbance of standard solution versus concentration of metal in parts per million (ppm), and the equation of each calibration curve derived. Typical calibration curves for tin and lead are shown in Figure 5.

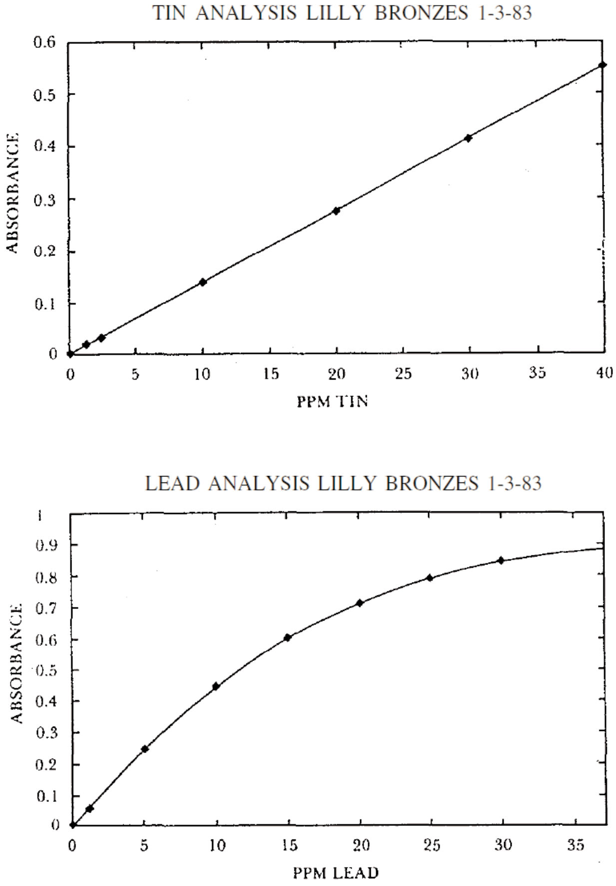

Figure 5. Atomic absorption calibration curves for tin and lead.

The precision and accuracy of the AAS methods were determined by duplicate analyses of five NBS and BCS alloys. A 10 ± 0.01 milligram portion of each alloy was weighed, dissolved in a the concentrated mixture, and diluted with distilled water to volume using a calibrated 50 mL volumetric flask. These standard alloy solutions were aspirated into the spectrophotometer, and the absorbance for one metal measured in all five solutions before re-setting instrumental conditions and going on to the measurement of the next metal. Tin was always determined first, because of its tendency to precipitate out of solution. Freshly prepared standard solutions were alternately aspirated in between the alloy solutions, and used to generate a new calibration curve for each analysis – thus preventing day-to-day instrumental variations and possible deterioration of standard solutions from influencing the analytical results.

Also, each standard and alloy solution was measured at several different times during the course of an analysis, which usually required about three hours, as a check on instrument stability. The whole procedure was performed twice, with new standard solutions being prepared, new portions of alloy being weighed out and dissolved, and new sets of calibration curves being plotted each time. In this way, the reproducibility and accuracy of the entire analytical method was determined.

The results of the duplicate analyses of the five NBS/BCS alloys, together with their known percentages of copper, tin, lead, and zinc, are presented in Table 2. It was again observed that the average of duplicate determinations provided better accuracy than single determinations. The average absolute error for these elements were calculated to be ± 1.52% for copper, ± 1.64% for tin, ± 2.12% for lead, and ± 2.99% for zinc. These are used to estimate the experimental uncertainty associated with each concentration value calculated.

One important fact can be concluded from the data in Table 2 – the AAS method is much more accurate than the AES method for the determination of these four elements. Experimental errors in the AAS analyses were about one tenth those encountered for the AES determinations.

The analyses of the Lilly Bronze samples followed exactly the procedure outlined for the analyses of the standard alloys. Results of these analyses are presented in Table 3 and discussed below.

Table 2. Atomic Absorption Analyses for Standard Alloys

Copper

	Percent calculated			
Element	**Trial 1**	**Trial 2**	**Average**	**Percent known**
BCS 364	80.53 ± 1.23	80.85 ± 1.24	80.69 ± 1.23	80.60
NBS 37D	71.31 ± 1.09	68.58 ± 1.05	69.95 ± 1.07	70.78
NBS 158	91.47 ± 1.40	92.17 ± 1.41	91.82 ± 1.40	90.86
NBS 124C	82.27 ± 1.26	87.11 ± 1.33	84.77 ± 1.30	84.22
BCS 207/2	88.10 ± 1.35	89.25 ± 1.33	88.68 ± 1.36	87.30

Tin

	Percent calculated			
Element	**Trial 1**	**Trial 2**	**Average**	**Percent known**
BCS 364	9.09 ± 0.149	9.30 ± 0.153	9.20 ± 0.151	9.30
NBS 37D	0.97 ± 0.0159	0.94 ± 0.0154	0.96 ± 0.0157	0.97
NBS 158	1.10 ± 0.0180	1.03 ± 0.0169	1.07 ± 0.0175	0.97
NBS 124C	4.79 ± 0.786	5.29 ± 0.868	5.04 ± 0.827	5.13
BCS 207/2	9.49 ± 0.156	9.66 ± 0.158	9.58 ± 0.157	9.74

Lead

	Percent calculated			
Element	**Trial 1**	**Trial 2**	**Average**	**Percent known**
BCS 364	9.21 ± 0.195	9.39 ± 0.199	9.30 ± 0.197	9.20
NBS 37D	0.92 ± 0.0195	0.92 ± 0.0195	0.92 ± 0.0195	0.94
NBS 158	< 0.17	< 0.17	< 0.17	0.004
NBS 124C	4.67 ± 0.099	5.05 ± 0.107	4.86 ± 0.103	4.74
BCS 207/2	0.71 ± 0.0151	0.71 ± 0.0151	0.71 ± 0.0151	0.70

Zinc

	Percent calculated			
Element	**Trial 1**	**Trial 2**	**Average**	**Percent known**
BCS 364	0.15 ± 0.0045	0.13 ± 0.0039	0.14 ± 0.0042	0.13
NBS 37D	26.79 ± 0.804	25.62 ± 0.769	26.21 ± 0.786	26.65
NBS 158	2.03 ± 0.0609	2.07 ± 0.0621	2.05 ± 0.0615	2.07
NBS 124C	4.87 ± 0.146	5.15 ± 0.155	5.01 ± 0.150	4.93
BCS 207/2	1.58 ± 0.0474	1.62 ± 0.0486	1.60 ± 0.048	1.60

Results of the Analyses

Fourteen objects were sampled. The elemental compositions of these alloys are presented in Table 3. Multiple samples were taken from three different objects; IMA# 60.32 had very small amounts of material removed from the vessel foot (sample #4), the mouth (sample #7), and from three separate sites on the cover (samples #10, 12, and 13). IMA# 48.13 was sampled at a site known to contain original alloy (sample #25) and also in an area that, from x-radiographic evidence, was suspected of being a later repair (sample #28). IMA# 60.288 was sampled at two different sites (samples #18 and 21).

Table 3. Element Compositions of Lilly Oriental Bronze Samples

		Percent element											
Sample	**Description**	**Cu**	**Sn**	**Pb**	**Zn**	**As**	**Ni**	**Fe**	**Mn**	**Si**	**P**	**Sb**	**Al**
1 (c) (foot rim)	48.115: Shang. 13–12th century	≤ 74*	≥ 15	≥ 10	< 0.03	>0.10	≤ 0.05	≤ 0.004	< 0.5	≤ 0.015	< 0.05	< 0.02	< 0.5
4 (a) (foot rim)	60.32 Eastern Zhou., early 5th century	≤ 74*	≥ 15	≥ 10	< 0.03	> 0.10	0.23 ± 0.047	0.071 ± 0.03	< 0.5	0.008 ± 0.004	< 0.05	0.17 ± 0.07	< 0.5
7 (c) (mouth)	60.32	76.0 ± 1.2	14.0 ± 0.23	2.86 ± 0.061	0.00055 ± 0.000017	> 0.10	0.17 ± 0.034	0.15 ± 0.07	< 0.5	> 0.015	< 0.05	0.19 ± 0.07	< 0.5
10 (a) (cover interior flange)	60.32	66.3 ± 1.0	11.7 ± 0.19	18.7 ± 0.40	0.0011 ± 0.00003	> 0.10	0.14 ± 0.028	0.22 ± 0.11	< 0.5	0.002 ± 0.001	< 0.05	0.18 ± 0.07	< 0.5
12 (a) (cover-edge)	60.32	n.d.	~ 50	~ 50	n.d.							~ 0.5–1%	
13 (b) (cover-ring)	60.32	~ 80–90	~ 5–10	~ 5–10	n.d.								
16 (b) (leg)	60.77 Zhou, 11th century	73.5 ± 1.1	13.1 ± 0.21	7.41 ± 0.16	0.009 ± 0.00027	> 0.10	≤ 0.05	1.3 ± 0.32	< 0.5	≥ 0.015	< 0.05	0.082 ± 0.030	< 0.5
18 (b) (leg)	60.288 Shang, 13–12th century	69.6 ± 1.1	16.9 ± 0.28	5.97 ± 0.13	0.007 ± 0.00021	> 0.10	< 0.05	0.068 ± 0.034	< 0.5	> 0.015	< 0.05	< 0.02	< 0.5
21 (d) (loop/handle)	60.288	~ 80–90	~ 5–10	~ 1–5	n.d.								
25 (b) (loop/handle)	48.13 Shang-Zhou 11th century	80.6 ± 1.2	12.3 ± 0.20	3.42 ± 0.73	0.013 ± 0.0004	> 0.10	< 0.05	0.05 ± 0.026	< 0.5	≤ 0.005	< 0.05	< 0.02	< 0.5
28 (b) (leg)	48.13	n.d.	~ 50	~ 50	n.d.							~ 0.5–1%	
31 (a) (bottom flange)	60.21 Zhou, 11–10th century	72.3 ± 1.1	11.9 ± 0.20	11.8 ± 0.25	0.026 ± 0.00078	≥ 0.10	< 0.05	0.21 ± 0.11	< 0.51	0.011 ± 0.005	< 0.05	0.071 ± 0.03	< 0.5
34 (a) (post)	60.288 Shang, 12th century	78.9 ± 1.2	12.4 ± 0.20	7.21 ± 0.15	0.102 ± 0.0031	0.065 ± 0.016	≤ 0.05	≤ 0.004	< 0.5	≤ 0.005	< 0.05	< 0.02	< 0.5
37 (b) (inch pin-end)	60.23 Western Zhou,	87.7 ± 1.3	7.32 ± 0.12	1.75 ± 0.37	0.006 ± 0.00018	> 0.10	< 0.05	0.025 ± 0.013	< 0.5	≥ 0.005	< 0.05	< 0.02	< 0.5
39 (a) (pin end)	60.158 Date uncertain	88.0 ± 1.4	1.26 ± 0.021	3.28 ± 0.070	0.004 ± 0.00012	≥ 0.10	0.31 ± 0.061	0.036 ± 0.018	< 0.5	< 0.005	< 0.05	< 0.02	< 0.5
43 (a) (ring interior)	60.161 Eastern Zhou, 5th century	72.4 ± 1.1	11.6 ± 0.19	13.1 ± 0.28	0.005 ± 0.00015	> 0.10	≤ 0.05	0.18 ± 0.027	< 0.5	< 0.005	< 0.05	0.082 ± 0.03	< 0.5
45 (b) (cover edge)	60.24 modern cover	95.6 ± 1.5	0.05 ± 0.0008	0.65 ± 0.013	0.123 ± 0.0037	0.065 ± 0.016	< 0.05	0.018 ± 0.009	< 0.5	0.009 ± 0.005	≤ 0.05	0.063 ± 0.03	< 0.5
51 (a) (foot)	60.44 Zhou 10th century	67.0 ± 1.0	10.9 ± 0.18	17.4 ± 0.37	0.007 ± 0.0021	0.066 ± 0.016	< 0.05	0.086 ± 0.043	< 0.5	< 0.005	< 0.05	< 0.02	< 0.5
53 (c) (leg)	60.34 Zhou, 10th century	79.9 ± 1.2	11.4 ± 0.19	5.77 ± 0.12	0.0145 ± 0.00044	> 0.10	< 0.05	≤ 0.004	< 0.5	0.005 ± 0.003	< 0.05	0.04 ± 0.02	< 0.5
57 (a) (foot rim)	60.43 Shang. 13–12th century	68.9 ± 1.1	6.47 ± 0.11	21.6 ±0.46	0.023 ± 0.00069	> 0.10	< 0.05	0.003 ± 0.0015	< 0.5	< 0.015	< 0.05	≥ 0.90	< 0.5

*Copper by difference

As is usually true when dealing with ancient materials, it was not possible to obtain absolutely clean, uncorroded alloy from these vessels in every case. However, an awareness of the extent of sample corrosion and/or contamination aided in the interpretation of the final analytical results. The relative purity of these samples was classified as being:

- Clean alloy – no corrosion and/or contamination
- Small amount of corrosion and/or contamination
- Medium to large amount of corrosion, or
- Large amount of corrosion to completely corroded

The designation of relative sample purity, and a general description of the site from which each sample was taken are indicated in the first column of Table 3. The second column contains the IMA accession number, and a brief description of the sampled vessel. Whenever possible, that is when at least 15 milligrams of sample was available, these materials were analyzed by both the atomic emission and atomic absorption methods. In these cases, only the more accurate AAS results for copper, tin, lead, and zinc are presented in the table. However, AES determinations of these four elements agreed with the AAS results in every case, within the experimental uncertainty of the AES method. The percentages of all the other elements (i.e., arsenic, nickel, iron, manganese, silicon, phosphorus, antimony, and aluminium) were determined by AES only.

Two samples (#25 and #57) were analyzed in duplicate by AAS – the average percentages obtained for Cu, Sn, Pb, and Zn are given in the table. All other compositional values in the table are the result of single determinations. Estimates of experimental uncertainty are also provided. Samples #1 and #4 were analyzed for all elements by AES only. A shortage of sample precluded AAS analyses. Also, samples #12, 13, 21, and 28 each weighed less than 5 milligrams, the minimum amount required for quantitative AES determinations. Therefore, 2.0 milligram portions of each of these were analyzed by AES and estimates of the amounts of Cu, Sn, Pb, and Zn present were obtained by visual comparison of their emission line intensities with those produced from vaporization of 2.0 milligram samples of NBS and BCS standard alloys.

Discussion of Analytical Results

With one exception, the modern cover of IMA# 60.24, all of the vessels analyzed proved to be leaded bronze. It is quite obvious from the results in Table III that all of the alloys contain only very small quantities of zinc. This is in accord with the findings of other reported bronze analysis studies which state that zinc was not used as a significant component of Chinese bronze alloys prior to the Han dynasty (206BC–220AD). It is almost certain that the small amounts of zinc found in the Lilly Bronzes were not intentionally added.

The main feature of the compositions of these alloys is their variability. Concentration of lead especially varies widely. No clear pattern of alloy composition is apparent and it would be premature to search for one since the number of vessels analyzed is presently too small to produce meaningful conclusions.

There are, however, certain observations that can be made. The cover from IMA# 60.24 has been identified as being of modern origin on the basis of stylistic considerations. X-radiographs of this cover reveal the lack of internal features (voids within the material) that are quite prominent in the vessel to which it supposedly belonged and that a piece of sheet copper was probably attached at a later time. The composition of sample #45 taken from the edge of this cover shows that it is almost pure copper, with practically no tin and very little lead and zinc present. That the composition of this material is completely different from those of the ancient alloys determined serves to reinforce the other observations made about the age of this object. Sample #28, from an area of IMA# 48.13 suspected of being previously repaired, has a composition of roughly equal amounts of tin and lead, with no copper or zinc detected, but does contain a small amount of antimony. This material is a soft solder and would be used for its properties of low melting point and ease of working when solid, properties of obvious value when used to carefully repair metal or alloy objects.

An interesting challenge in interpretation of the analytical results is posed by the multiple samples taken from IMA# 60.32. Material from the mouth of this vessel (sample #7) has a much lower lead content than the sample taken from the foot (sample #4). It therefore seems possible that the foot of this vessel was cast separately, using an alloy of different composition. In addition, the cover of this vessel is stylistically different from the vessel body. This cover, from which three samples were removed (sample #10, 12 and 13), is also of a different composition than the body. Sample #10 contained much more lead than did the body of the vessel, and thus resembles the alloy taken from the foot more than it does the body alloy. The cover was also shown to contain "repaired" areas (by x-radiography). Sample #12, from one of these areas, has a composition of about 50% tin/50% lead, with no copper or zinc in evidence, but again containing a small amount of antimony. Sample #13 was so corroded, and of such small size, that we can only say that the alloy was once a leaded bronze.

It is apparent that materials analysis data, in combination with x-radiographic and art historical evidence, can be quite helpful in answering specific questions such as those discussed above. However, general conclusions about ancient metallurgical practices require not only accurate analytical methods, but most importantly, the availability of a large body of authentic objects that can be sampled and studied. The results presented here represent only the first phase of a continuing art historical/material analysis study of this most interesting group of ancient Chinese artifacts.

Acknowledgements

We wish to thank Mr. Lawrence Hipsher of Detroit Diesel-Allison Division, General Motors Corporation, for help in the production and interpretation of the x-radiographs, and Dr. Douglas E. Shrader of Varian Associates Inc. for allowing us to use their Atomic Absorption Spectrophotometer in these studies. The contributions of Dr. David Malik, Rebecca Love, and Mrs. Barbara McDaniel (Department of Chemistry, Indiana University – Purdue University at Indianapolis) in developing the computer programs are also greatly appreciated.

We finally would like to thank the Oriental Department for making available for study the authentic bronze vessels of the Eli Lilly Collection.

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Printed in the USA
November 1, 2010
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