Archaeometallurgical chemistry 1870-1920: the high point of gravimetric analysis

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ABSTRACT: This paper continues an earlier contribution that summarized the publications in archaeometallurgical chemistry from 1790 to 1869. Selection for inclusion is focussed primarily on papers which include the chemical analyses of archaeological non-ferrous metals (overwhelmingly copper alloys), but related reports of metal mining and processing, and discussions of metal supply and trade, are also included. The result is a list of 744 publications between 1870 and 1920, of which 29 papers each report more than 30 chemical analyses. The full list and a transcription of the chemical data from approximately 75 papers are available on the FLAME website (http://flame.arch.ox.ac.uk/ public-resources/historical-metal-data-2/). All of the analyses discussed here were produced by gravimetric (wet chemical) analyses, which, from the late 19th century onwards, could be argued to be the best analyses available until very recently, taking into account the relatively large sample taken and the ability to use the analytical total as a quality check.

Introduction

A previous paper (Pollard 2013) attempted to summarize publications from the period 1790 to 1869 containing the chemical analyses of archaeological copper alloy objects. The start date was determined by the earliest known publication (initially thought to be Dizé 1790), and the end date was adopted because it marked the first major publication of a summary of such analyses, by Dr Ernst Freiherr von Bibra (1806-1878). This summary contained 1250 analyses, of which 600 were his own, and the other 650 were taken from the earlier work of at least 90 different analysts (von Bibra 1869). Subsequent research (Pollard 2015) showed that analyses before 1790 had been carried out by Stanesby Alchorne (1727-1800) at the Mint in London, and were reported in Pownall (1775). They were not fully described, however, and it is not clear whether they were qualitative or quantitative. Most recently (Pollard 2018a), it has been shown that the earliest known published quantitative analyses of archaeological copper alloy appear to be those of Johan Christian Wiegleb (1732-1800), who, in 1777, described in some detail the analyses of four archaeological copper objects for tin and silver.

This further work (Pollard 2018a) has also shown that the original list of papers published before 1869, then numbering 118, is a substantial underestimate. An updated and consolidated list of these publications, currently numbering 305, is now available at http://flame.arch.ox.ac.uk/public-resources/historical-metal-data/, alongside a digitized spreadsheet of the data contained in the larger publications before 1869.

The period 1870 until 1920

The start date obviously follows on from the previous contribution. The end date is chosen from a consideration of two factors. One is obviously the end of the First World War (1914-1918), which convulsed western Eurasia, and caused immense social as well as scientific change. The date of 1920, however, marks the last year before the first publication of the analysis of archaeological metal by the new method of emission spectroscopy (Baudoin 1921). This introduction of instrumental methods of chemical analysis marked a step-change in analytical chemistry, certainly in terms of the speed of analysis, and also in the range of elements it was possible to measure.

However, all of the analyses discussed in this paper were produced by the 'humid method', originally developed in the late 18th century, but gradually refined to become the method of gravimetric analysis. At the beginning of the 19th century, such analyses generally only measured a few elements in copper (usually tin, and perhaps lead and silver), but by the end of that century up to ten or more elements were routinely reported. Providing the copper is directly measured (and not estimated by difference), then the analytical total is a highly sensitive measure of the quality of these analyses, and totals between 99.5 and 100.5% are routinely recorded, indicating extremely high quality analyses. Some of the leading 20th century archaeometallurgists (especially Earle Caley) continued to use gravimetric analysis into the 1960s, believing it to be superior to contemporary instrumental methods. It has to be said that, in the hands of a skilled analyst, and for elements present at greater than a few tenths of a percent, these gravimetric analyses are probably as reliable (if not more so) than modern analyses produced on micro-samples, since the larger sample requirements reduce the effects of inhomogeneity in the sample.

The database collated for this period is, unsurprisingly, much larger than that compiled for the period before 1870, at least in terms of the number of publications. The full list (http://flame.arch.ox.ac.uk/public-resources/historical-metal-data-2/1870-1920-table.docx) contains approximately 744 publications, compared to 300 from before 1870. As with the earlier list, not all the listed papers contain chemical analyses – some are included because they relate to non-ferrous and non-precious metal mining history. Others contain important points of discussion, such as the origins of tin bronze, considered further below. Transcriptions of the chemical data reported in the literature of the period, where the number of analyses reported in an individual paper is greater than approximately 10, can be found at http://flame.arch.ox.ac.uk/public-resources/historical-metal-data-2/Historical-Data-1870-1920.xlsx. The spreadsheet currently contains data from 79 papers, with a total number of analyses of approximately 3,643 (ignoring duplication). Table 1 lists 29 papers, each containing more than 30 analyses, in this period. The largest is Chassaigne and Chauvet (1904), with 520 analyses, of which around 55 are from bronzes found in the Départment de la Charente, but the remainder are a summary of previously published data from all over the world. Interestingly, in terms of the numbers of published analyses, the Excel data file for the period 1790-1869 contains 2,855, and that for 1870-1920 is only slightly larger, despite containing data from more publications. These two totals cannot be directly compared since neither compilation includes all the analyses for the period, and the duplication caused by later authors either republishing their own data, or reproducing other analyst's data, is not taken into account. Nevertheless, it does suggest that the *rate* of publication of chemical data does not change much through the 19th century. This is probably a reflection of the fact that gravimetric analysis is relatively slow and laborious.

Giants of archaeometallurgical chemistry from 1870 to 1920

The 50 years from 1870 to 1920 are dominated by a number of major figures, some of whom are now more often remembered for their overall contributions to other disciplines, but were actually central to the development of archaeological chemistry. In France, the leading scholar was the chemist and politician Pierre Eugène Marcellin Berthelot FRS (1827-1907). Berthelot is now known for his work on thermochemistry, and the synthesis of organic compounds from inorganic materials, thus disproving the notion that organic chemistry was fundamentally related to living organisms. He was the leading chemist in France in the late 19th century, being elected as one of the 'Forty Immortals' of the Académie Française (Jungfleisch 1913). He became fascinated by the history of alchemy, and, from 1884, translated and commented on many alchemical sources, including manuscripts in Greek, Egyptian, Arabic, Persian and Indian (cf Berthelot 1885; 1887-8). Perhaps it was this interest in the chemistry of the ancient world that led to him to apply his expertise in analytical chemistry to the material remains recovered by archaeology. His first contribution was to analyse wine sealed in a glass vessel (Berthelot 1877), but he subsequently analysed many metal assemblages from Europe, Egypt and the Near East. A compendium of this work was published in a single volume in 1906 under the title *Archéologie et histoire des sciences*. His biography and complete bibliography of publications was compiled by Jungfleisch (1913).

Leading contributors in the UK included Percy and Gowland. John Percy FRS (1817-1889) trained in medicine but eventually became Professor of Metallurgy at the Metropolitan School of Sciences (London), the Royal School of Mines (London), and at the Royal Artillery Institution (Woolwich). He is best known for his volumes on *Metallurgy: the art of extracting metals from their ores, and adapting them to various purposes of manufacture* in four volumes: Vol I. *Fuel; fire-clays; copper; zinc; brass, etc*. (Percy 1861) (revised and enlarged edition 1875); Vol II. *Iron and steel* (Percy

Table 1: Publications between 1870 and 1920 containing more than 30 analyses.

Date	Reference	No of analyses
1874	Napier J 1874, *Manufacturing arts in ancient times, with special reference to Bible history* (Hamilton, Adams and Co, London).	43
1881	Evans J 1881, *The ancient bronze implements, weapons, and ornaments of Great Britain and Ireland* (Longmans, Green and Co, London).	35
1886	Blümner H 1886, *Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römern*, Vol 4 (B G Teubner, Leipzig).	78
1886	Much M 1886, *Die Kupferzeit in Europa und ihr Verhältnis zur Kultur der Indogermanen* (Kaiserlich-Königlichen Hof- und Staatdruckerei, Wien).	53
1892	Roberts-Austen W C and Wingham A 1892, *Report on the analysis of various examples of oriental metal-work, &c., in the South Kensington Museum and other collections* (South Kensington Museum, London).	82
1894	Chauvet G 1894, 'Une cachette d'objets en bronze découverte à Vénat, Commune de St. Yrieux près Angoulême', *Bulletin et mémoires de la Société archéologique et historique de la Charente* 4, 141-292.	33
1894	Gowland, W 1894, 'On the art of casting bronze in Japan', *Annual Report of the Board of Regents of the Smithsonian Institution*, 609-651.	46
1895	Helm O 1895, 'Chemische Untersuchung westpreussischer vorgeschichtlicher Bronzen und Kupferlegirungen, inbesondere des Antimon-gehaltes derselben', *Zeitschrift fur Ethnologie* 27, 1-24	50
1897	Gladstone J H 1897, 'On the transition from the use of copper to that of bronze', *Journal of the Anthropological Institute of Great Britain and Ireland* 26, 309-320.	39
1897	Kröhnke O 1897, *Chemische Untersuchungen an vorgeschichtlichen Bronzen Schleswig-Holsteins* (Peters, Kiel).	45
1898	Girard C 1898, 'Bronze. IV. Technologie', *La Grande Encyclopédie: inventaire raisonné des sciences, des lettres et des arts* 8, 139-149.	39
1898	Montélius O 1898, 'Die Chronologie der ältesten Bronzezeit in Nord-Deutschland und Skandinavien', *Archiv für Anthropologie* 25, 443-483.	30
1900	Montélius O 1898, 'Die Chronologie der ältesten Bronzezeit in Nord-Deutschland und Skandinavien', *Archiv für Anthropologie* 26, 1-40, 459-511, 905-1012.	75
1903	Chassaigne L and Chauvet G 1903, *Analyses de bronzes anciens du Départment de la Charente* (L Picat, Ruffec).	520
1904	Ambrosetti J B 1904, *Arqueología argentina: El bronce en la region Calchaquí* (Alsina, Buenos Aires).	30
1904	Bezzenberger A 1904, *Analyse vorgeschichtlicher Bronzen Ostpreußens* (Gräfe und Unzer, Konigsberg).	109
1906	Berthelot M 1906, *Archeologie et histoire des sciences* (Gauthier-Villars, Paris).	36
1906	Gowland W 1906, 'Presidential address: copper and its alloys in prehistoric times', *Journal of the Anthropological Institute of Great Britain and Ireland* 36, 11-38.	49
1906	Hammer J 1906, Der Feingehalt der griechischen und römischen Münzen (Dissertation, Tübingen).	364
1907	de Mortillet A 1907, 'Bronze in South America before the arrival of the Europeans', *Annual Report of the Smithsonian Institution 1907*, 261-266.	50
1908	Mosso A 1908, *Le armi più a antiche di rame e di bronzo* (Tipografia della R Accademia dei Lincei, Rome).	64
1908	von Miske K 1908, *Die Prähistorische Ansiedelung Velem St. Vid, Band I: Beschreibung der Raubbaufunde* (Konegen, Wien).	152
1912	Gowland W 1912, 'Copper and its alloys in early times. Presidential address', *Journal of the Institute of Metals* 7, 23-49.	66
1915	Mathewson C H 1915, 'A metallographic description of some ancient Peruvian bronzes from Machu Picchu', *American Journal of Science* 40, 525-616.	33
1915	Mead C W 1915, 'Prehistoric bronze in South America', *American Museum of Natural History, Anthropological Papers* 12(2), 15-52.	166
1919	de Créqui-Montfort G and Rivet P 1919, 'Contribution a l'étude de l'archéologie et de la métallurgie colombiennes', *Journal de la Société des Américanistes de Paris* 11, 525-591.	251
1919	Koga N 1919, 'A table of the chemical analysis of old Japanese and Chinese copper coins assayed by Mr. Koga', *Kokogaku Zasshi (Journal of the Archaeological Society of Nippon)* 9(7), 35-52.	113
1919	Reinglass P 1919, *Chemische Technologie der Legierungen. 1ster Teil, Die Legierungen mit Ausnahme der Eisen-Kohlenstofflegierungen* (Spamer, Leipzig).	180
1920	Chikashige M 1920, 'Ancient oriental chemistry and its allied arts', *Man* 20, 161-168.	32

1864) (2nd edition 1875); Vol III. *The metallurgy of lead, including desilverization and cupellation* (Percy 1870), and Vol IV. *Metallurgy. Silver and gold* (Percy 1880). The first three of these volumes were republished as facsimiles by De Archaeologische Pers in association with the Historical Metallurgy Society. Percy's promised volume on *Tin, nickel, cobalt, antimony, bismuth, arsenic, platinum, and other metals applied in the arts* was never published. The published volumes arose from a desire to record metallurgical practice in the 19th century, since it was clear that many of the processes, some surviving from medieval or even earlier practices, were being lost. Significant as these volumes were, Percy's publications as technical appendices to some of the most important excavation reports of the day, such as those of Austin Henry Layard at Nineveh and Babylon (Layard 1853) and Heinrich Schliemann at Mycenae and Tiryns (Schliemann 1878), were equally important, providing some of the first 'specialist reports' in archaeology. Percy's metallurgical collection was given to the South Kensington Museum in London, and was catalogued by Blake (1892). A more recent examination of the collection was published by Cackett (1989).

William Gowland (1842-1922) was a mining engineer, metallurgist and archaeologist. He spent the years 1872-1888 in Japan, where he worked at the Osaka mint, advising on refining and alloying copper for coinage. Whilst in Japan, he conducted and published many archaeological surveys and excavations of burial mounds, including imperial mausolea. Some of the material collected by him was donated to the British Museum via Sir Wollaston Franks, now forming part of its Japanese and Korean collections. On his return to England he became involved with archaeological work, including excavations at Silchester, and, in 1901, was charged with raising one of the leaning sarsens at Stonehenge. Between 1902 and 1909 he taught metallurgy at Imperial College, London, and became their first Emeritus Professor of Metallurgy in 1907. He was a Fellow of the Royal Society, Vice-President of the Society of Antiquaries between 1902 and 1906, Chairman of the Royal Anthropological Institute between 1905 and 1907, and President of the Institute of Mining between 1907 and 1908. The Japanese Government made him a Chevalier of the Order of the Rising Sun on his departure from Japan, and he has been referred to as the 'Father of Japanese Archaeology'. His many published chemical analyses are of the highest quality, and several of his publications uniquely combine his knowledge of Japanese and European metallurgy (*eg* Gowland 1899).

It is noteworthy, however, that the largest contribution in this (as well as the preceding) period comes from German-speaking scholars, especially Virchow, Helm and Olshausen. Rudolf Ludwig Carl Virchow (1821-1902) was a physician, pathologist, anthropologist and prehistorian. Trained in medicine, he became the first Chair of Pathological Anatomy at the University of Würzburg in 1849, and subsequently the first Chair of Pathological Anatomy and Physiology at Berlin University. Besides his many medical and public health contributions, he had a profound influence on anthropology and archaeology through his editorship of the journal *Zeitschrift für Ethnologie*, published by the German Anthropological Association and the Berlin Society for Anthropology, Ethnology and Prehistory, which Virchow co-founded and founded in 1869 and 1870 respectively. He edited this journal from its founding in 1866 until his death in 1902. His interest in anthropology dates to 1865, when he discovered pile dwellings in northern Germany, and he subsequently led a major excavation of the hill forts in Pomerania. He undertook several archaeological and anthropological field trips to Asia Minor, the Caucasus, Egypt, and Nubia, sometimes in the company of Heinrich Schliemann. His total publications are said to number more than 2000.

A very significant development during this period took place in Berlin on 1 April 1888 – the establishment of the Chemical Laboratory for the Royal Museums in Berlin under its first director Friedrich Rathgen (1862-1942), who retained the position until his retirement in 1927 (Riederer 1976; Gilberg 1987). He was primarily interested in improving the methods employed for the conservation of museum objects, but he also worked on the scientific examination and chemical analysis of art-historical objects and researched their production techniques. This was the first scientific laboratory directly concerned with the chemical study of museum and archaeological artefacts.

Another noteworthy aspect of the contributions to archaeometallurgical chemistry in this period are the first publications by female scientists. The earliest and most distinguished is that in 1876 of the prehistoric archaeologist Johanna Mestorf (1828-1909). She was given an honorary post at the Kiel Museum in 1868. In 1873 this museum was merged into the Museum vaterländischer Alterthümer, the forerunner of the Schleswig-Holstein State Archaeological Museum, and also of the Institute for Prehistory and Ancient History at the University of Kiel. In 1891 she succeeded the director, becoming the first female museum director in Germany. In 1899 the Prussian Ministry of Culture made her an honorary professor. Her archaeological work was supported by Virchow, amongst others, and her publications in *Zeischrift für Ethnologie* often contained chemical analyses by Olshausen. In the French literature, the first female contribution so far noted is that of Clémence Royer (1830-1902), who is principally remembered for her translation of Darwin's 'Origin of Species' into French, but in 1870 she became the first woman to be elected to a French scientific society (Société d'Anthropologie de Paris) and published frequently in the Bulletin of that society (*eg* Royer 1886).

An important archaeometallurgical event that occurred in 1912 was the publication of the first widely-available English translation of Agricola's *De Re Metallica* of 1556 (Hoover and Hoover 1912). Noted for its remarkable woodcuts of mining and smelting, the extensive footnotes by the Hoovers on all aspects of the ancient metallurgical processes provided the best summary of early metallurgy since the works of Percy (1861-1880), and only surpassed 50 years later in the work of Tylecote (1962; 1976; 1987). Perhaps even more remarkably, one of the editors, Herbert Clark Hoover (1874-1964), subsequently served as the 31st President of the United States (1929-1933).

New directions in archaeometallurgical chemistry during 1870-1920

The remit of archaeometallurgical chemistry continued to expand during this period. For example, the first reports appear on the chemical analysis of metallurgical slags (*eg* Cermak 1887). Similarly, the first metallographic analyses of archaeological metals appeared. Following the first publication of the metallography of modern iron (Sorby 1864), Giolitti (1911), Foote and Buell (1912) and Garland (1913) reported the metallography of copper alloys from Italy, Peru and Egypt respectively. Also during this period, more detailed studies appeared focussing on the corrosion of archaeological bronzes (*eg* Schuler 1879, Fletcher 1887), and the relationship between corrosion processes and environmental factors began to be seriously studied (*eg* Berthelot 1894).

Equally significant, the prehistoric metalwork of new parts of the world began to be analysed and published, particularly for the New World. Such studies include work on the pre-Columbian metalwork of the United States of America (Putnam 1883a; Moore 1903) and Mexico (Putnam 1883b; de Nadaillac 1883; Wibel 1887; Fiske 1911). Pre-Columbian South America (particularly Peru, Bolivia and Argentina) is represented by the work of Forbes (1870), Ambrosetti (1904) and Baessler (1904). Although the analysis of Chinese material had occurred very early in the history of archaeometallurgical chemistry (Klaproth 1807), the earliest data on complex Japanese alloys such as *Shakudo* appeared later in the 19th century (Pumpelly 1866). The interest in East Asian metals continued through studies by European scientists (*eg* Kalischer 1875; Gowland 1894; Morin 1874; Roberts-Austen and Wingham 1892), but these were soon followed by contributions from east Asian scholars, such as Sato (1900) and Chikashige (1920). Similarly, the study of Russian metalwork began relatively early through the work of European scholars (*eg* Clarke 1810), and studies by Russian scientists began in the mid-19th century (*eg* Uvarov 1855; Popov 1873). In the Indian sub-continent, analyses only began in 1877 (Jagor 1877), and were continued by various European scientists, with analytical data by Indian scholars only starting in 1918 (Neogi 1918). An important contribution, however, was made by Praphulla Chandra Ray (1861-1944); he published two volumes on *A History of Hindu Chemistry* (Ray 1902; 1909) in which he translated many manuscripts into English, including commentaries on the extraction of zinc (Ray 1909, 4; see also Ball 1881 and 1886-7 for details of the Indian production of zinc).

As noted above, the earliest spectrographic analyses of archaeological bronzes appear to be the work of Baudouin (1921) and Weiss *et al* (1923). The principles of spectroscopic analysis were first published by Kirchoff and Bunsen (1860), following the earlier observation that each element produces a distinctive series of emission lines in the visible (and infrared) region of the electromagnetic spectrum. Precise measurement of the wavelength of these lines can be used to identify which elements are present in the sample, and quantification can be achieved by measuring their intensity and calibrating the intensities against standards. Initially such measurements were made by passing an electric spark through a gas, but eventually a spectroscope was devised which passed a spark between two solid electrodes, one of which was formed from the sample. The emitted light was dispersed by a quartz prism, and the position and intensity of the emission lines recorded on a photographic plate. There was relatively early adoption of the technique in the iron industry (Parry and Tucker 1880), but it took several decades for it to be applied to archaeological material.

Perhaps most importantly, however, the period 1870 to 1920 saw the emergence of some of the questions that have dominated archaeometallurgy for the subsequent 150 years. As discussed elsewhere (Pollard 2018b), the question of the determination of the provenance of metals (tracing metal to ore source) first emerged in the 1840s (Göbel 1842) but became the dominant research question by the end of that century. Specifically, the origin of tin bronze alloys, and the sourcing of the required tin, emerges as an important discussion point during this period. William Kirby Sullivan (1821-1890) provides an important contribution on this topic in O'Curry (1873). Other key publications on the origins of alloying include those of de Mortillet (1875) and Gladstone (1897). Early discussions on the sources of the tin include von Baer (1876), Royer (1886), Bapst (1886; 1888) and Berthelot (1887a; 1887b).

The first appearance of zinc in copper alloys is also discussed. Göbel (1842) had already noticed that Roman metal contained zinc, whereas Greek did not. Diergart (1902) and Tabaries de Grandsaignes (1907) both discuss early occurrences of zinc in copper alloys, and several scholars discuss the history of zinc extraction and processing (*eg* Frantz 1881; Hofmann 1882; Browne 1916).

Conclusions

The period 1870 to 1920 saw a large growth in the number and range of papers concerned with the chemistry of archaeological copper alloy objects. By the end of the 19th century, the method of gravimetric analysis was generally of a very high standard, and these data are perhaps the most representative analyses ever produced of archaeological copper alloys, in terms of the major and minor components. Apart from the publication of new data, many papers discussed the history of mining and the sources of the various metals involved in copper alloys. The questions addressed and the range of countries studied expanded dramatically over the period. Perhaps equally important from a historical perspective was the fact that a number of extremely eminent chemists contributed to the study of archaeological materials, addressing a range of archaeologically significant questions. As signified by the titles of a number of publications (*eg* Berthelot 1906; Neumann 1907), the collaboration between chemistry and archaeology was now well established.

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