The first hundred years of archaeometallurgical chemistry: Pownall (1775) to von Bibra (1869)

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ABSTRACT: This paper compiles and reviews the chemical analyses of archaeological copper alloy metalwork from the earliest documented attempts around 1775 to the first major compilation by von Bibra in 1869. The early analyses (up to around 1845) are often incomplete even for the major alloying elements (Sn, Zn, Pb), and rarely report any trace element data, but by the 1850s gravimetric analyses often include up to 10 elements or more, and are therefore as complete as many modern analyses. The large samples taken (1g of metal), whilst not in line with modern practice, does mean that the analyses are likely to be minimally affected by inhomogeneity and surface enrichment phenomena, which can be a problem with modern micro-analyses. This paper is based on approximately 110 publications between 1775 and 1869. The published data from the major contributions have been digitized and are available on the RLAHA website.

Pre-1775: The art of assaying and the touchstone

According to Vitruvius' *De Architectura Libri Decam*, written around the 1st century BC, King Hiero of Syracuse, after gaining power, wished for a golden crown to be made as a votive offering for the Gods (Granger 1931-34, Book IX 9-12). He gave a weighed amount of gold to the goldsmith, and a crown was duly delivered. Subsequently, a charge was made that the gold had been adulterated with silver to cheat the king, and Archimedes (287-212 BC) was asked to investigate the matter. He knew that the specific gravity of the crown would show whether the gold had been adulterated with silver (SG Au 19.3, SG Ag 10.49). However, the volume of the crown could not be measured without re-melting it – a classic 'non-destructive analysis' challenge of the sort very familiar to modern analysts! While taking a bath, he famously noticed that the water overflowed as he got in the tub – the more his body sank into the water the more water ran out over the tub – and he realized that the displacement of water could be used to measure the volume of the crown, and hence calculate the density. Following experiments with gold and silver of equal weights to the crown, he was able to calculate the amount of silver in the crown, and hence reveal the fraud. This is almost certainly the first documented non-destructive analysis of a metal object.

Long before Archimedes, and probably stretching back almost to the first use of metals, the art of assaying the chemical composition of precious metal objects had been practised. Assaying is essentially testing by fire – the oxidative removal of the more volatile metals and oxides, and the separation of gold from silver by cupellation. Greenaway (1962) emphasises that assaying is the oldest quantitative chemical technique, and contains the origins of modern analytical chemistry. Assaying can be traced using written sources back to at least early Mesopotamia (early 2nd millennium BC), where cuneiform tablets describe in some detail the quantitative assay of gold and silver (Levey 1959, 182, 190), but even then these techniques were old. One of the earliest medieval descriptions of assaying and parting gold from silver is to be found in the writings of Geber (Abu Mūsā Jābir ibn Hayyān, *c*AD 721-815), whose works were translated into English by Richard Russel in 1678 (Holmyard 1928). By the 12th century AD in England, assaying the fineness of silver was an essential part of the work of the Mint (Greenaway 1962), and this must have been true elsewhere at the time. It was probably also true since the formal adoption of metal discs as money sometime during the first millennium BC (Greenaway 1964). A number of surviving European medieval texts give us increasingly clear descriptions of the process of assaying, both of metal objects and, in the case of base metals, of the ores from which they come. Book III of Theophilus' *On Divers Arts* (*c*1110-1140 AD; Hawthorne and Smith 1963) is more of a metal-workers manual, but it does describe ways to recover gold from scrap gilded metal, and also how to part gold from silver. The first western book to give a clear description of assaying is the *Probierbüchlein*, written by an unknown German goldsmith or assayer around AD1520 (Sisco and Smith 1949). Lazarus Ercker's *Beschreibung allerfürnemisten mineralischen Ertzt und Berckwercksarten* (1574; Sisco and Smith 1951) rapidly became the European textbook on such matters. Ercker (1528-1594) was appointed assayer at Dresden in 1554 and in 1567 tester of coins at Kutná Hora, near Prague. His book was originally published in German at Prague in 1574, and was reprinted in 1580, 1598 and 1629. It was widely translated across Europe, including an English version published by Sir John Pettus (1683) as *Fleta Minor, or, the Laws of Art and Nature in Knowing, Judging, Assaying, Fining, Refining and Inlarging the Bodies of Confined Metals.* The first part of this work is a translation of Ercker's volume in five books, four of which describe assaying metal and 'oars' in detail:

Book 1: 'of Silver Oars'
Book 2: 'of Gold Oars and Gold Slicks'
Book 3: 'of Copper Oars'
Book 4: 'of Lead oars, Tin, Antimony, Quick-Silver, Iron, Steel and Load-stone'
Book 5: 'of Salt-Petre'

Probably equally as old as assaying is the art of using the touchstone to assess the fineness of precious metals, especially gold (Oddy 1986). A touchstone is a flat piece of dark fine grained stone upon which the metal to be tested is rubbed. For gold, the colour of the streak is indicative of the purity of the gold, since both silver and copper present in the gold will change the colour. Theophrastus (*c*371-*c*287 BC), in his book '*On Stones*' (*c*315 BC; Caley and Richards 1956, 54), says that 'The nature of the stone which tests gold is remarkable, for it seems to have the same power as fire, which can test gold too'. The precision of the assay can be improved by comparing the streak from a coin or object with those taken from standard alloys. From the calculations made by Oddy (1986) based on Theophrastus' text, the touchstone could detect one part in 144 of impurity in the gold, which, if true, was a precision not surpassed until modern times. The antiquity of the touchstone is unclear. Oddy (1986, 164) says that the first certain reference is in the 6th century BC, but the fact that it was so well known in Theophrastus' time, and that it is also referred to in Sanskrit texts contemporary to Theophrastus, suggests that it is much older than this. Others have suggested an Egyptian origin, but even this may be conservative. It continued in use through the medieval period in Europe, and is still used by modern coin collectors.

Analysis by 'the humid method'

The origins of analytical chemistry as we understand it today are to be found in the late 18th century, when trial by fire gave way to 'the humid method', or precipitating known compounds out of solutions, giving rise to quantitative gravimetric analysis. In 1739 Johan Andreas Cramer (1710-1777), working at the University of Leiden, had published *Elementa Artis Docimasticae* (Cramer 1741), which promulgated the idea of the *menstruum*, which is the medium in which chemical reactions take place, rendering reactions possible by separating the parts of the reactants to allow them to combine to give products (Greenaway 1962, 92). This interest in aqueous chemistry rapidly led, through the increasingly systematic study of aqueous chemical reactions and precipitations by Robert Boyle, Étienne François Geoffroy and others, to the publication in 1777 by Torbern Bergman (1735-1784) at the University of Uppsala, Sweden, of a protocol for the aqueous gravimetric analysis of gemstones. This was followed by subsequent but more detailed protocols by Nicolas-Louis Vauquelin (1763-1829) in Paris (1799) and Martin Heinrich Klaproth (1743-1817) in Berlin (1792/3). The analytical protocols of these three chemists have been re-published and compared by Oldroyd (1973).

The earliest analyses of archaeological metal

Klaproth is usually credited as the first analyst to publish data on archaeological metal, citing his detailed record of the gravimetric analysis of six Greek and nine Roman copper alloy coins, as well as a careful description of each coin (Klaproth 1792/3). This paper, entitled *Mémoire de numismatique docimastique*, was presented at the Royal Academy of Sciences and Belles-Lettres of

Berlin on 9 July 1795, but the volume was not published until 1798 (but is dated 1792/3). (Klaproth's publications are often equally confusing to follow: Riederer (1980, 7) lists some relevant to archaeometallurgy, but a comprehensive list is given in Anon (2002)). Although Klaproth specifically devised a methodology for analysing copper alloys (discussed in detail by Caley (1949)), he was not actually the first 'archaeometallurgical chemist' (Pollard 2013). This honour appears to go to by Michel Jean Jérome Dizé (1764-1852), who published in 1790 the analyses of eight copper alloy coins, given to him by M L'abbé Antoine Mongez (1747-1835). These consisted of five Roman coins (subsequently identified by Mongez (1804) as dating to after the emperor Nero), one Greek ('de Syracuse' according to Mongez) and two 'Gaulish' coins. The analyses were gravimetric, but reported only the amount of tin present in the alloy.

However, further investigation reveals that this might not be the first, either. Although not archaeological, the earliest report of the quantitative chemical analysis of any metal appears to be that of Gustav von Engeström (1738-1813), a Swedish mineralogist and chemist and a student of Bergman's, who became 'Assessor of Mines' in Sweden. In 1776 von Engeström published a paper on the chemical analysis of the mysterious imported white copper (paktong) from China, which he found to contain copper and nickel (with some cobalt), and gave the proportion of nickel to copper as 5 or 6 parts to 13 or 14 (*ie* approximately 29% Ni; Liu *et al* 2015). More significantly for this paper, we also get a tantalising hint of the chemical analysis of a 'sword… found in a bog at Cullen, in the County of Tipperary, in Ireland', in a paper read by Governor Pownall at the Society of Antiquaries (London) on 10 February 1774 (Pownall 1775). He says:

> 'That the Society might have a precise and philosophic description of the metal, I applied to the master of the mint; and by his direction Mr. Alchorn, his Majestie's assay-maker, made an accurate assay of the metal'.

Mr Alchorn reports:

> 'It appears to be chiefly copper, interspersed with particles of iron, and perhaps some zinck, but without containing either gold or silver: it seems probable, that the metal was cast in its present state, and afterward reduced to its proper figure by filing. The iron might either have been obtained with the copper from the ore, or added afterwards in the fusion, to give the necessary rigidity of a weapon. But I confess myself unable to determine any thing with certainty.'

We may assume that 'Mr Alchorn' is Stanesby Alchorne (1733-1800), who was assistant to Joseph Harris, Mint-Master, in 1757, and became the King's assay-master in 1789. Mr Alchorne should perhaps receive the accolade of being the first person we know of to chemically assay an archaeological copper artefact, but the qualitative nature of his report probably leaves Dizé as the true pioneer archaeometallurgical chemist.

The main purpose of this paper is to document the chemical study of archaeological copper alloys from these first steps to the first major compilation of chemical analyses published by Baron Ernst Freiherr von Bibra (1806-1878) in 1869. Von Bibra published approximately 1250 analyses, of which 600 were his own, and the other 650 were taken from earlier work by at least 90 other analysts. Although each analysis is attributed to an individual analyst, von Bibra does not give the original reference, and so one of the aims of this work is to make available all these analyses in digital format, and to cross-reference them as far as possible with the original publications, noting differences where they exist. This task was greatly aided by a near-contemporary publication to that of von Bibra, by Wibel (1865, 10-18), who listed a large number of publications (46 between 1790 and 1861) containing the chemical analyses of archaeological copper alloys, but gave no data. The only challenge Wibel's listing presents to the contemporary scholar is that the abbreviation system used for journal titles in the 19th century is sometimes extremely obscure – several have changed their names many times, and there was a great tendency to publish translations of the same paper in a number of different journals. Nevertheless, it has proved possible to identify the source of most of von Bibra's data.

Assembling the archive

Table 1 lists (in date order) all the papers so far located between 1790 and 1869 which contain analytical data on (primarily) archaeological copper alloy objects – some contain assays of silver and gold, but these do not provide an exhaustive list of such analyses. The title of the journal is given in full as it was at the date of publication, to allow others researchers to find the publication more easily. An associated Excel database ('Historical Metallurgy. Data 1790-1869', available at http://flame.arch.ox.ac.uk/public-resources/historical-metal-data/) transcribes all the analyses from papers that contain more than around five analyses, and cross-references them to earlier publications where relevant, noting any differences between the original and the reproduced values. I have attempted to reproduce the original descriptions of the object analysed, but some have been shortened, and I have not translated them from the original German, French or Swedish. Anybody wishing to use these data should refer to the original publications rather than rely on these transcriptions. Naturally, all

Table 1: A compilation of works published up until 1869 which contain quantitative chemical analyses of archaeological copper alloy objects.

Date	Reference	Analyst (if different)	No of analyses
1775	Pownall T 1775, 'An account of some Irish antiquities', *Archaeologia* 3, 355-370.	Alchorn	
1775	von Engeström G 1775, 'Försök på naturlig flos zinci ifrån China', *Kungliga Vetenskaps Academiens Handlingar* 36, 78-85.		
1776	von Engeström G 1776, 'Pak-fong, en chinesisk hvit metal', *Kungliga Vetenskaps Academiens Handlingar* 37, 35-38.		
1776	von Engeström G 1776, 'Pak-Fong, ein Chinesisches weiss metal', *Der Königlichen Schwedischen Akademie der Wissenschaften neue Abhandlungen, aus der Naturlehre, Haushaltungskunst und Mechanik* 38, 40-42.		
1790	Dizé M J J 1790, 'Analyse du cuivre, avec lequel les Anciens fabriquoient leurs médailles, les instruments tranchans', *Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts* 36, 272-276. (also listed as *Journal de Physique*, April 1790).		8
1792-3	Klaproth M H 1792 and 1793, 'Mémoire de numismatique docimastique', *Mémoires de l'Academie Royale des Sciences et Belles-Lettres depuis l'avénement de Fréderic Guillaume II au Trône. (Classe de Philosophie Expérimentale)*, 97-113 (published Berlin 1798).		15
1796	Pearson G 1796, 'Observations on some metallic arms and utensils; with experiments to determine their composition', *Philosophical Transactions of the Royal Society of London* 86, 395-451.		7
1797	Hjelm P J 1797, 'Om konsten at håra Koppar', *Kungliga Vetenskaps Academiens nya Handlingar* 18, 98-110.		
1797	Klaproth M H 1797, 'Analyse chimique de la masse métallique d'un miroir antique', *Mémoires de l'Academie Royale des Sciences et Belles-Lettres depuis l'avénement de Fréderic Guillaume II au Trône. (Classe de Philosophie Expérimentale)*, 14-22 (published Berlin 1800).		
1799	Hjelm P J 1799, 'On the art of hardening copper', *Philosophical Magazine* (Series 1) 5, 271-278.		1
1799	Dizé M J J 1799, 'Mémoire sur la séparation, par la voie humide, du zinc uni a cuivre, alliage connu sous la dénomination de cuivre jaune, de laiton et de similor; suivi d'une analyse de cinq espèces de monnoies de cuivre, grecques et romaines', *Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts* 48, 173-183.		5
1804	Mongez A 1804, 'Mémoire sur le bronze des anciens et sur une épée antique', *Mémoires de l'Institut National, Classe de littérature et beaux-arts* 5, 187-228.	Darcet jun and Dizé	10
1804	Mongez A 1804, 'Mémoire sur l'épée gauloise, et sur les procédés que les anciens ont suivis pour convertir le fer en acier', *Mémoires de l'Institut National, Classe de littérature et beaux-arts* 5, 517-555.		
1804	Mongez A 1804, 'Second mémoire sur le bronze antique, sur des épées et un anneau élastique des anciens', *Mémoires de l'Institut National, Classe de littérature et beaux-arts* 5, 496-516.	Darcet jun	5
1806	Thomson T 1806, 'On silver coins', *Journal of Natural Philosophy, Chemistry and the Arts* 14, 396-409.		
1807	Klaproth M H 1807, 'Chemische untersuchung der metalmasse antiker eherner Waffen und Geräthe', *Journal für die Chemie, Physik und Mineralogie* 4, 351-363.		7
1807	Klaproth M H 1807, 'Untersuchung chinesischer münzen' *Journal für die Chemie, Physik und Mineralogie* 4, 449-451.		2
1809	Thomson T 1809, 'Mémoire sur les monnoies d'argent', *Annales de Chimie* 71, 113-136.		
1810	Klaproth M H 1810, 'Chemische untersuching der metalmasse der chinesischen gong-gong's', *Journal für die Chemie, Physik und Mineralogie* 9, 408-409.		1
1810	Fabbroni G 1810, 'Del bronzo ed alter leghe conosciute in Antico' *Atti dell'Accademia Italiana di Scienze, Lettere, ed Arti* 1, 203-245.		
1812	Klaproth M 1812, 'Memoire sur la docimasie des medailles', *Annales de Chimie* 81, 82-97.		
1813	Thomson T 1813, 'Analyse de l'instrument chinois, appelé gong ou tam-tam', *Annales de Chimie* 89, 42-53.		

Table 1 continued

Date	Reference	Analyst (if different)	No of analyses
1813	Thomson T 1813, 'Analysis of the Chinese gong', *Annals of Philosophy* 2, 208-210.		
1815	Klaproth M H 1815, *Chemische Abhandlungen Gemischten Inhalts* (Nicholaischen Buchhandlung, Berlin und Stettin) [Vol 6 of *Beiträge zur Chemischen Kenntniss der Mineralkörper*].		32+8
1816	von Humboldt A 1816, *Vues des Cordillères, et Monumens des Peuples Indigènes de l'Amérique*, Vol 1 (Paris).	Vauquelin, p 314	1
1817	Clarke E D 1817, 'Observations upon some Celtic remains, lately discovered by the public road leading from London to Cambridge, near to the village of Sawston, distant seven miles from the University', *Archaeologia* 18, 340-343.		5
1818	Anon (Mongez A) 1818, 'Mémoire sur l'étain des Romains', *Histoire et Mémoires de L'Institut Royal de France, Classe d'histoire et de littérature ancienne* 3, 23-25.		
1821	Clarke E D 1821, 'An account of some antiquities found at Fulbourn in Cambridgeshire, in a letter addressed to Nicholas Carlisle, Esq. F.R.S. Secretary', *Archaeologia* 19, 56-61.		
1822	Fyfe A 1822, 'Analysis of tutenag, or the white copper of China' *Edinburgh Philosophical Journal* 7, 69-71.		
1824	Vauquelin N L 1824, 'Analyse du metal de la statue trouvée à Lillebonne, près Causebec, department de la Seine-Inférieure, dans un terrain appartenant à M. Holley', *Annales de Chimie et de Physique* 25, 395-401.		
1826	Davy J 1826, 'Observations on the changes which have taken place in some antient alloys of copper', *Philosophical Transactions of the Royal Society of London* 116, 55-59.		
1826	Davy J 1826, 'Über die veränderungen, welche in einigen kupferlegierungen der alten statt gefunden haben', *(Frorieps) Notizen aus dem Gebiete der Natur- und Heilkunde* 13, 183-184.		
1826	Feneulle H 1826, 'Analyse des monnaies d'argent romaines, trouvées à Famars', *Annales de Chimie et de Physique* 32, 320-327.		
1826	Seyffarth G 1826, 'Einige bemerkungen über die so genannten Hünergraber, als beitrag zur Unrgeschichte Deutschlands', *Beiträge zur vaterandischen Altherthumskhunde* 1, 81-99.		
1827	Hünefeld L and Picht F 1827, *Rügens metallische Denkmäler der Vorzeit, vorzugsweise chemisch bearbeitet, und als Beitrag zur vaterlandischen Alterthumskunde herausgegeben* (Leopold Voss, Leipzig).		10
1827	Mongez A 1827, 'Troisieme mémoire sur le bronze des anciens et sur sa trempe', *Histoire et Mémoires de l'Institut Royal de France, Académie des Inscriptions et Belles-Lettres* 8, 363-369.		
1827	Walchner F 1827, 'Vermischte Beiträge. I. Untersuchung einiger römischen münzen, die im Jahre 1825 auf dem Quettich zu Baden-Baden gefunden wurden', *Jahrbuch der Chemie und Physik* 21, 204-209.		
1830	Wilhelmi K 1830, *Beischreibung der Vierzehen alten Deutschen Todtenhügel* (Joseph Engelmann, Heidelberg).	'Apotheker Greiff'	
1831	Mongez A 1831, 'Mémoires sur l'art du monnoyage chez les anciens et chez les modernes', *Histoire et Mémoires de l'Institut Royal de France, Académie des Inscriptions et Belles-Lettres* 9, 187-265.		
1832	Girardin J 1832, 'Note sur la composition de l'alliage qui forme la cloche d'argent renfermée dans le beffroi de Rouen', *Annales de Chimie et de Physique* 50, 205-212.		
1832	Schubarth L 1832, *Handbuch der technischen Chemie* (Rücker and Püschler, Berlin).	Darcet, pp 312, 313 etc	
1833	Julian S 1833, 'Procédé des Chinois pour fabriquer les tam-tams et les cymbales', *Annales de Chimie et de Physique* 54, 329-331.		
1836-7	Berzelius J 1836-7, 'Undersökning af metallmassen i några fornlemningar', *Annaler for Nordisk Oldkyndighed,* 104-108.		10
1836-9	Kruse F K H 1836-9, 'Resultate einiger untersuchungen über die alterthümer in Livland, Curland und Esthland', *Mémoires de la Société Royale des Antiquaires du Nord*, 354-360.	Forchhammer, Göbel	
1838	Jahn F 1838, 'Zusammensetzung eines stücks metall, gefunden in einem Hünengrabe bei einödhausen in der Nähe der alten Bergruine Henneberg', *Annalen der Pharmacie* 27, 338-341.		
1841	Landerer X 1841, 'Archäologisch-chemische mittheilungen', *Repertorium für die Pharmacie* 73, 369-382.		

Table 1 continued

Date	Reference	Analyst (if different)	No of analyses
1842	Göbel F 1842, *Ueber den Einfluss der Chemie auf die Ermittelung der Völker der Vorzeit oder Resultate der chemischen Untersuchung metallischer Alterthümer insbesondere der in den Ostseegouvernements vorkommenden, Behuss der Ermittelung der Völker, van welchen sie abstammen* (Ferdinand Enke, Erlangen).		119
1842	Kruse F 1842*, Necrolivonica,* Beilage F. (Voss, Leipzig)	Göbel, Klaproth, Picht und Hünefeld, Berzelius, Forchhammer, Dizé, Landerer, Thomson, D'Arcet	84
1843	Erdmann O L 1843, 'Ueber antike münzen', *Journal für praktische Chemie* 30, 334-343.		
1844	von Santen H L and Lisch G C F 1844, *Chemische Analysen antiker Metalle aus heidnischen Gräbern Mecklenburgs, mit antiquarischen Einleitungen und Forschungen begleitet von G. C. F. LISCH* (Schwerin).		15+14+2
1844	Webb T H 1844, 'Accounts of a discovery of antiquities made at Fall River, Massachussetts, communicated by Thomas H. Webb, M.D. in letters to Charles C. Rafn, Secretary, with remarks by the latter', *Mémoires de la Société Royale des Antiquaires du Nord 1840-1843*, 104-119.	Berzelius, Forchammer	
1845	Elsner L 1845, 'Ueber die chemische zusammensetzung eines Chinesischen metallspiegels', *Journal für praktische Chemie* 34, 443-446.		
1845	Fresenius R 1845, 'Chemische analyse einer Celtischen waffe', *Annalen der Chemie und Pharmacie* 53, 136-138.		
1845	Moëssard A 1845, 'Analyse de divers coins de bronze antiques, trouvés dans le department de l'Oise', *Comptes rendus hebdomadaires des séances de l'Académie de Sciences* 21, 1177-1179.		7
1846	Moëssard A 1846, Analyse verschiedner alter bronzestücken (coins), welch im department de l'Oise gefunden wurden', *Journal für Praktische Chemie* 37, 255-256.		
1846	Knapp F 1846, 'Untersuchung einer antiken bronze', *Annalen der Chemie und Pharmacie* 58, 104-106.		
1846	Pelouze J 1846, 'Mémoire sur un nouveau mode de dosage de cuivre', *Annales de Chimie et de Physique* 16, 426-435.		
1846	von Estorff G O C 1846, *Heidnische Alterthümer der Gegend von Uelzen im ehemaligen Bardengaue (Königreich Hannover)* (Hahn'sche Hof-Buchhandlung, Hannover).	Bodemann	
1847	Diamond H W 1847, 'Account of wells *or* pits, containing Roman remains, discovered at Ewell in Surrey', *Archaeologia* 32, 451-455.	Faraday	
1847	Erdmann O L 1847, 'Zusammensetzung einiger altgriechischen bronzemünzen', *Journal für praktische Chemie* 40, 371-374.	Mitscherlich, Schmid, Wagner, Monse, Marchand, Ulich	8
1847	Julian S 1847, 'Alliages de cuivre, cuivre blanc, gong et tam-tams', *Comptes Rendues Hebdomadaires des Séances de l'Académie des Sciences* 24, 1069-1070.		
1847	von Dürrich F and Menzel W 1847, *Die Heidengräber am Lupfen (bei Oberflacht)* (Arnold's Buchbruderei, Stuttgart).	Fehling	
1848	Berthier P 1848, *Traité des essais par la voie sèche*, Vol 2 (Auguste Durand, Paris).	Vauquelin	
1848	Onnen H 1848, 'Untersuchung einiger sorten von chinesischen kupfer', *Journal für Praktische Chemie* 44, 242-244.		
1849	Cooke T L 1849, 'On bronze antiquities found at Dowris, in the King's County', *Proceedings of the Royal Irish Academy* 4, 423-440.	Donovan O'Sullivan	

Table 1 continued

Date	Reference	Analyst (if different)	No of analyses
1849	Mallet J W 1849, 'Report on the chemical examination of antiquities from the Museum of the Royal Irish Academy', *Transactions of the Royal Irish Academy* 22, 313-342.		18+8+8
1850	Donovan M 1850, 'On the analysis of the gold-coloured bronze antiquities found at Dowris, King's County', *Proceedings of the Royal Irish Academy* 4, 463-470.		
1850	Sabatier J and Sabatier L 1850, *Production de l'or, de l'argent et du cuivre chez les anciens et hôtels monétaires des Empires Romain et Byzantin* (Bellizard, Saint-Péterbourg).		
1850	Salvétat L 1850, 'Analyse de deux bronzes antiques de l'époque gallo-romaine', *Annales de Chimie et de Physique* 30, 361-365.		
1851	Wilson D 1851, *The archaeology and prehistoric annals of Scotland* (Sutherland and Knox, Edinburgh).	Wilson G, p 246; Davy E, p 47	8
1852	Berlin N J 1852, 'Några materialier för bedömandet af sammanhanget mellan de antika bronsernas sammansättning och ålder', *Annaler for Nordisk Oldkyndighed og Historie*, 254-271.		25
1852	Berlin N J, 'Om några nordiska metall-legeringars sammansättning', *Annaler for Nordisk Oldkyndighed og Historie*, 249-254.		193
1852	Bobierre A 1852, 'Untersuchungen über die dauerhaftigkeit der bronze als schiffsbeschlag', *Dingler's Polytechnische Journal*, 187-191.		
1852	Girardin J 1852, 'Analyse de plusieurs produits d'art d'une haute antiquité', *Mémoires présenté par divers savants à l'Academie des inscriptions et belles-lettres de l'Institut de France* (series 1) 2, 86-104.		4
1852	Mallet J W 1852, *Account of a chemical examination of the Celtic antiquities in the collection of the Royal Irish Academy Dublin* (University Press, Dublin).		
1852	Phillips J A 1852, 'A chemical examination of the metals and alloys known to the ancients', *The Quarterly Journal of the Chemical Society of London* 4, 252-300.		37
1852	Phillips J A 1852, 'Untersuchungen einiger münzen und waffen der alte', *Annalen der Chemie und Pharmacie* 81, 207-218.		
1852	Rossignol J-P 1852, *Mémoire sur le métal que les anciens appelaient Orichalque* (Ch Lahure, Paris).		
1853	Girardin J 1853, 'Analyse sehr alter kunstprodukte', *Journal für praktische Chemie* 60*,* 89-94.		22
1853	Hawranek J 1853, 'Chemische zusammensetzung eines mergels und eines hippuritenkalkes aus der Gosau, so wie einiger antiker bronzen', *Journal für praktische Chemie* 60, 443-444.		
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1853	Pratobevera E 1853, 'Ueber den celtischen character der Judenburger antiken', *Mittheilungen des historischen Vereines für Steiermark* 4, 54-72.	Gottlieb	
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1853	Wocel J 1853, 'Archäologische parallelen', *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften. Philosophisch-Historische Classe (Wien)* 11*,* 716-761.		
1854	Wocel J E 1854, *Archäologische Parallelen* (Kaiserlich-Königlichen Hof- und Staatsdruckerei, Wien).	Hawranek, Liebich, Görgey, Hlasiwetz, Quadrat, Adam	
1855	Wocel J 1855, 'Archäologische parallelen', *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften. Philosophisch-Historische Classe (Wien)* 16, 169-227.		
1855	Uvarov A S 1855, *Recherches sur les antiquités de la Russie méridionale et des Côtes de la mer Noire* (Ouvaroff , St Pétersbourg).		

Table 1 continued

Date	Reference	Analyst (if different)	No of analyses
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1857	Erdmann O L 1857, 'Vermischte mittheilungen. 6: Antike bronzen aus Oldenber', *Journal für praktische Chemie* 71, 213-215.	Künzel	4
1857	Phillips J A and Darlington J 1857, *Records of mining and metallurgy: or facts and memoranda for the use of the mine agent and smelter* (E and F N Spon, London).		
1857	Pratobevera E 1857, 'Archäeologische beiträge', *Mittheilungen des historischen Vereines für Steiermark* 7, 185-200.	Buchner, p 197	
1857	von Rauch A 1857, 'Über die römischen Silbermünzen und den innern Werth desselben', *Mitteilungen der Numismatischen gesellschaft zu Berlin* 3, 282-308.		
1858	Genth F A 1858, 'Contributions to metallurgy, No. 1', *Journal of the Franklin Institute* 36, 261-266.	Pöpplein	10
1858	Weinhold K 1858, 'Über ein zu straßengel aufgedecktes grab', *Mittheilungen des historischen Vereines für Steiermark* 8, 140-150.	Gottlieb, p 143	
1860	von Fellenberg L R 1860, 'Analysen von antiken bronzen', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 444-446, 43-56; Nr 448-449, 65-79; Nr 459-460, 153-162.		60
1860	Troyon F 1860, *Habitations Lacustres des temps Anciens et Modernes* (Bridel, Lausanne).	Bischoff, pp 113, 152-3	
1861	von Fellenberg L R 1861, 'Analysen von antiken bronzen', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 474-475, 41-55; Nr 490-491, 173-187.		40
1861	Roux B 1861, 'Observations sur des canons chinois et cochinchinois', *Comptes Rendues Hebdomadaires des Séances de l'Académie des Sciences* 52, 1046-1050.		4
1861	Schrötter A 1861, 'Die chemischen bestandtheile der bronzen in den gräbern von Hallstatt und ihre beziehung zu deren ursprung', *Sitzungsberichte der philosophisch-historische classe der Akademie der Wissenschaften* 37, 174–181.		
1861	Schrötter A 1861, *Die chemischen Bestandtheile der Bronzen in den Gräbern von Hallstatt und ihre Beziehung zu deren Ursprung* (Kaiserlich-Königlichen Hof- und Staatsdruckeri, Wien).	Binko, p 56	
1861	Weinhold K 1861, Grab-alterthümer aus klein-glein in Untersteiermark', *Mittheilungen des historischen Vereines für Steiermark* 10, 265-296.	Gottlieb	
1862	Abel F A and Field F 1862, 'Some results of the analysis of commercial coppers', *The Quarterly Journal of the Chemical Society of London* 14, 290-303.		
1862	von Fellenberg L R 1862, 'Analysen von antiken bronzen (Fünfte Fortsetzung Von Nr 101 bis 120 inclusive)', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 497-498, 1-14.		20
1862	Wilson D 1862, *Prehistoric Man. Researches into the origin of civilisation in the Old and the New World*, Vol 1 (Macmillan, Cambridge)	(pp 310, 312)	
1863	Commaille A 1863, 'Mémoire sur la composition des monnaies et médailles romaines antiques' *Journal de Pharmacie et de Chimie* 44, 5-13.		44
1863	von Fellenberg L R 1863, 'Analysen von antiken bronzen', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 531-532, 43-54; Nr 548, 135-142.		40
1863	Wibel F 1863, *Beiträge zur Kenntniss antiker Broncen von Chemischem Standpuncte* (Hamburg).		
1864	von Fellenberg L R 1864, 'Analysen von antiken bronzen', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 566-567, 122-134.		20
1865	Bischoff E 1865, *Das Kupfer und seine Legirungen* (Julius Springer, Berlin).		
1865	Church A H 1865, 'Analyses of some bronzes found in Great Britain', *The Journal of the Chemical Society of London* 18, 215-217.		4
1865	von Fellenberg L R 1865, 'Analysen von antiken bronzen', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 580-581, 1-20.		21

Table 1 continued

Date	Reference	Analyst (if different)	No of analyses
1865	Wibel F 1865, *Die Cultur der Bronze-Zeit Nord- und Mittel-Europas* (Kiel).		
1866	Kopp E 1866, 'Examen chimique d'ornements retirés de tombes celtiques découvertes dans les tumulus de la forêt de Mackwiller (bas-Rhin, arrondissement de Saverne)', *Bulletin de la Société Chimique de Paris* 5, 99-103.		
1866	von Fellenberg L R 1866, 'Nachtag zu den analysen antiker bronzen', *Mittheilungen der Naturforschenden Gesellschaft in Bern* Nr 613, 261-264.		
1866	Struve H 1866, 'Analyse verschneidener antiker Bronzen und Eisen aus der Abakan- und Jenissei-Steppe in Siberien', *Bulletin de l'Académie impériale des Sciences de St-Petersbourg* 9 282-290.		
1867	Stolba F 1867, 'Analyse alterthümlicher bronzeobjecte aus der sammlung des böhmischen museums', *Journal für praktische Chemie* 101, 139-145.		
1868	Flight W 1868, 'On the chemical composition of a Bactrian coin', *Numismatic Chronicle* 8, 305-308.		
1869	von Bibra E F 1869, *Die Bronzen und Kupferlegirung der alten und ältesten Völker, mit Rücksichtnahme aur jene der Neuzeit (*Ferdinand Enke, Erlangen).		1249

analyses are gravimetric. Some authors have given the weights of each precipitate, but others only record the calculated compositions. For the early data, often only tin is quantified, but by Klaproth's compilation of his own data in 1815, values are usually given for Cu, Sn, Pb, Zn, Fe, Ag and Au (but not in all samples). von Bibra himself routinely reports Cu, Sn, Zn, Pb, Ag, Fe, Sb, As, Ni, Co, S, and occasionally Au. Often the analytical totals are reported as 100%, which gives rise to the suspicion that Cu may have been determined by difference (this is sometimes explicitly noted), or, less likely, that the data have been normalised. The best data are those where a true analytical total is given, and often this is between 99 and 101%, indicating a very good analysis. It is not always possible, however, to know exactly what elements were sought but not found, or simply not sought. Some elements are reported as 'trace', and it can be estimated from other data from the same analyst for that particular element what this might mean numerically. Sometimes however, trace elements are reported together in the original publication, but not noted as such in subsequent publications.

The most significant publications in terms of the total number of analyses quoted are those of Klaproth (1815) (32 copper alloy analyses and 8 silver alloys), Göbel (1842) (119 analyses, of which 55 are his own and 32 are repeated from Klaproth), Berlin (1852) (25 of his own and 121 from previous authors), von Fellenberg (1860, 1861, 1862, 1863, 1864, 1865) (201 of his own analyses), and von Bibra himself.

There appear to be numerous errors of transcription in the publications which report previous analyses, so anybody interested in theses analyses should always check with the original publication as far as possible. Likewise, there sometimes seem to be errors of attribution – most notably in the case of Dizé, where Klaproth (1815), Göbel (1842) and von Bibra (1869) all give three of his analyses, which they attribute to Dizé (1790) when they do not occur there, but are in Dizé (1799). Similarly, there are some omissions which, from this distance, appear inexplicable. For example, von Bibra reproduces 22 of Klaproth's analyses, whereas the original publication has 32. Likewise, he lists 45 of Göbel's analyses, out of a total of 55. Other compilations do the same. It is not obvious why the ones listed were chosen over the others. It does however mean that von Bibra's list, for example, cannot be taken as comprehensive of all of the earlier analyses.

Assessing the legacy

Apart from historical interest (since these publications do represent analytically and intellectually the first approximately 100 years of archaeometallurgical chemistry), what value, if any, do these data have today? It is commonplace in our computerized era to dismiss any analyses not carried out in the last few decades (and to ignore any papers which are not immediately available by bibliographic search). This is unwise. Intellectually, for example, we can trace back to Göbel in 1842 the theory of the chemical provenancing of archaeological metals, and, although it has subsequently evolved, it has remained largely unchanged until very recently (Pollard *et al* 2014). Obviously, and particularly for the analyses carried out before the mid-19th century, the analyses are incomplete, sometimes even for the major elements. Only if Cu, Sn, Zn and Pb are all reported can we expect to use the data to classify the alloy type. But, at least by 1850, many analyses carry information on most of the trace elements routinely reported today by electron microprobe or XRF. No quality assurance data is ever given – there appears to be no concept of standards, and nor are detection limits reported (although this could also be said of many more recent analyses!). The analytical total, where quoted and not artificially forced to be 100%, does give a good indication of the overall quality of the analysis, but does not help to pinpoint errors with specific elements. In all the literature reviewed here, only one paper (Phillips 1852) explicitly and systematically analysed each object twice and reported the average – in other words, we have very little perception of how representative are the given analyses. On the other hand, most analyses would have started with a sample consisting of around a gram of metal, so perhaps heterogeneity was less of problem than it can be today. The phenomenon of lead segregation is a well-known limitation for many modern micro-sampling techniques, whereas in gravimetry, with a large sample and the precipitation of all the lead, this would have been much less of an issue. A vivid example of the problems of sampling inhomogeneity caused by lead segregation is given by Hughes *et al*'s (1982) reanalysis of the Middle-Late Bronze Age material published by Brown and Blin-Stoyle (1959).

Table 1

Analysis by Klaproth of a Greek Bronze Coin of Syracuse and a Recent Analysis of a Coin from the Same Locality

Element	*Klaproth's analysis, %*	*Recent analysis, %*
Copper	87.2	85.14
Lead	7.5	7.13
Tin	4.9	7.43
Iron	0.4	0.08
Nickel	...	0.03
Arsenic	...	0.10
Sulfur	...	Trace
	100.0	99.91

Table 6

Analysis by Klaproth of the Metal from an Ancient Mirror and a Later Analysis by Bibra of the Metal of an Ancient Roman Mirror

Element	*Klaproth's analysis, %*	*Bibra's analysis, %*
Copper	62	64.46
Tin	32	28.36
Lead	6	7.13
Iron	...	Trace
Nickel	...	0.05
	100	100.00

Figure 1: Comparison of Klaproth's analyses with later analyses (after Caley 1949).

The accuracy of Klaproth's data has been indirectly tested by Caley (1949), as shown in Figure 1 and Table 2. Caley's table 1 compares Klaproth's analysis of a Greek 3rd century BC coin from Syracuse (sample 30 A 1 in the attached database transcription of Klaproth's data from 1815, which is also analysis No 1 in Klaproth (1792)) with a 'recent analysis' (by Caley himself, also using gravimetry). Obviously the coin analysed by Caley was not the same as that of Klaproth (and differed slightly in date), but the correspondence between the two is respectable, with the main difference being Sn (4.9% for Klaproth, 7.43% for Caley) and Fe (0.4% and 0.08%). Caley also concluded (1949, 243) that:

> 'from what is now known about the variation in composition of Greek coinage bronze with time, it should be expected that the coin he [*ie* Klaproth] analysed would contain a lower proportion of tin and a higher proportion of lead than the one analysed by the writer [*ie* Caley]'. He continues: 'As regards the minor components ..., Klaproth was also in error, since ... he failed to find most of them, and probably obtained an incorrect result for the only one he did find.'

Caley's tables 2 and 6 compare Klaproth's analyses with those of similar objects analysed by von Bibra. Table 6 is inconclusive, since it compares two different Roman mirrors analysed by Klaproth [analysis No 64 VI on the sheet 'Klaproth 1815' in the on-line 'Historical Metallurgy Data 1790-1869' spreadsheet noted above (originally derived from Klaproth 1797)] and von Bibra [Römische Waffen, Schmuck und andere Gegenstände No 4 on the sheet 'Bibra 1869']. We note that von Bibra also analysed other similar mirrors [*eg* Römische Waffen, Schmuck und andere Gegenstände No 3, with 71.6% Cu, 22.7% Sn, 4.8% Pb and 0.27% Zn], so beyond agreeing that mirrors have higher tin, we cannot draw any conclusions about the reliability of Klaproth's analysis. Caley's table 2 is, however more instructive (Table 2). The original compares a Roman orichalcum coin (Claudius, emperor AD 41-54) analysed by Klaproth [33 B 12 on the sheet 'Klaproth 1815' (derived from Klaproth 1792, No 12)] with an identical coin (same denomination) analysed by von Bibra [Römische Kaisermünzen No 27 on the sheet 'Bibra 1869']. Caley draws the obvious conclusion – Klaproth was remarkably accurate for copper and zinc, but failed to quantify a range of trace elements, which would almost certainly have been there. Added to this table are the average values and standard deviations for the analyses of Claudian orichalcum coins, based on 18 analyses produced largely by Giles Carter and colleagues using XRF (data compiled by Pollard *et al* in prep). This shows that both Klaproth and von Bibra are within the ranges for copper and zinc, and the traces of von Bibra are just about within range apart from nickel.

Table 2: Comparison of Klaproth's and Caley's data for a Claudian coin (Caley 1949, table 2) with an average analysis of the same issue from modern data.

Element	Klaproth's analysis	Later analysis (von Bibra)	Modern average	Modern std dev
Cu	77.9	77.44	79.8	4.3
Zn	22.1	21.5	19.7	3.8
Sn		0.3	0.12	0.12
Pb		trace	0.34	0.34
Fe		0.32	0.35	0.35
Ni		0.24	0.02	0.06
Sb		0.2	0.08	0.06
S		trace		
(As)			0.03	0.01

One major limitation, however, on using any of these data is the lack of precision in the identity and description of the objects sampled. For most publications, the description is limited to something like 'a Celt found at Bordesholm (Holstein)'. Never is a museum accession number given, so the possibilities of tracking down these objects to modern collections are very slight. Rarely, a drawing of the object concerned is provided, offering the possibility of a more accurate typological assignment. Likewise, as would be expected of 19th-century archaeology, chronology is weak and mostly absent. An object is often simply described as either 'Roman' or 'Celtic'. The exceptions to these limitations are the analyses of coins, of which there are many. Most coins are usually attributed to a particular ruler, so a good chemical chronology could be constructed from these data.

Earle Caley (1900-1988) was one of the leading historians of archaeometallurgical chemistry in the 20th century. It is interesting to note that his own analytical work was done using gravimetry, even as late as the 1960s – he clearly preferred gravimetry to the instrumental method available at the time (optical emission, using a variety of electrode configurations). In his compilation of analyses of ancient metals (Caley 1964) he devotes 13 pages to a detailed description of gravimetric methods for the analysis of copper alloys and corrosion products (pp 81-93), compared to five on emission spectrography (pp 93-97). This preference for gravimetry over emission spectroscopy is to some extent justified, particularly for the major alloying elements tin and lead, as shown in Figure 2. This shows a plot of %Sn vs %Pb for von Bibra's data above, and below the same plot for the optical emission analyses of the British and Irish Early Bronze Age copper objects published by the SAM project (Junghans *et al* 1960; 1968; data compiled by Bray (2009)). Whilst the comparison is not archaeologically meaningful, since von Bibra contains data on a wide range of archaeologically-disconnected samples, it does show an artificial upper limit of around 10% tin in the SAM OES data which is clearly not there in the gravimetric determinations of the late 19th century. The OES limit is due to the difficulties in quantifying the intensity of the Sn emission line on a photographic plate when tin is high, under conditions which are set for the simultaneous measurement of the trace elements.

Conclusion

In summary, there is a wealth of analytical data up to and including that published by von Bibra in 1869. The early work of Dizé, Pearson and, to a lesser extent, that of Klaproth and Göbel, is limited by the range of elements sought, since it often only includes one or two of the alloying elements. By 1850, however, gravimetric analysis included most of the elements reported today – for example, Mallet (1849) reported Cu, Sn, Pb, Zn, Fe, Co, Au, Ag, As, Sb and S, and analytical totals of between 99.32% and 100.47%. Totals of this accuracy are rarely achieved today, and the relatively large sample taken ensures that issues such as surface enrichment and bulk inhomogeneity are unlikely to be problematic. Apart from issues with some trace elements, analyses

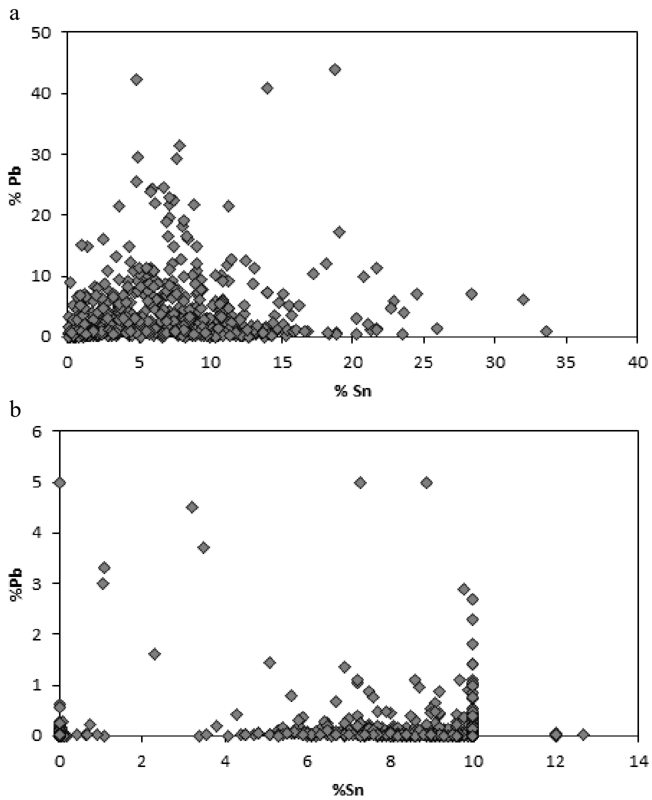

Figure 2: Plot of tin vs lead a) all data published by von Bibra (1869) using gravimetry, b) a similar plot using the SAM data (recompiled by Bray 2009) measured by optical emission spectrometry.

done between 1850 and 1950 are probably as good as many analyses currently available, but, of course, at a higher cost in terms of sample, and potentially lacking archaeological contextual data of the quality required today. With care, they are still useable, and given that, for various reasons, many of these objects are no longer available for analysis, they should not be forgotten.

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