

The Chemical Composition of Brass in Nuremberg Trombones of the Sixteenth Century

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Brass is an alloy of copper (Cu) and zinc (Zn). Because it is malleable, durable, solderable, and not thermosetting (i.e., it does not cure irreversibly), it is an ideal material for the construction of brasswind musical instruments. Its mechanical and physical properties are affected primarily by the amount of zinc present in the material.¹ The chemical composition of the alloy, and especially the ratio of zinc to copper, is thus an extremely significant parameter in the manufacturing process. Unfortunately, there is little detailed information on the chemical composition of brass alloys in pre-1600 brasswind musical instruments; consequently many questions arise as to the material one should use in making reproductions of such instruments. The present study does not attempt to answer this question definitively; rather its objective is to shed some light on the subject by means of a systematic X-ray fluorescence (XRF) analysis of nine sixteenth-century Nuremberg trombones (Table 1). These instruments have been analyzed, along with their crooks, tuning bits, and associated mouthpieces.

collection	inv. no.	manufacturer	date
Germanisches Nationalmuseum (Nuremberg)	MI170	Erasmus Schnitzer	1551
Museum of Pilgrimage and Local History (Altötting)		Anton Schnitzer I	1576
Accademia Filarmonica (Verona)	13.301	Anton Schnitzer I	1579
Palais Lascaris (Nice)	CIII	Anton Schnitzer I	1581
Museum für Hamburgische Geschichte (Hamburg)	1928/328	Conrad Linczer	1587
Hessisches Landesmuseum (Kassel)	1905/161	Anton Schnitzer II	1593
Edinburgh University (Edinburgh)	2695	Anton Schnitzer II	1594
Germanisches Nationalmuseum (Nuremberg)	MI167	Anton Drewelwecz	1595
Bayerisches Armeemuseum (Ingolstadt)	10699	Anton Schnitzer II	1598

Table 1: The sixteenth-century Nuremberg-made instruments under consideration.

Nuremberg sheet brass of the sixteenth century

Sixteenth-century Nuremberg brass differs considerably from contemporary brass in its metallurgical properties, particularly as regards the ratio of copper to zinc. Moreover,

sixteenth-century brass is a characteristically inhomogenous material that includes several trace elements. Among these, lead (Pb) is the most significant one, as it affects the mechanical properties of the material to a considerable degree. Different raw materials as well as different production processes were employed in the manufacture of early brass. Modern manufacturers use the direct process, melting the two principal elements of copper and zinc directly into each other, but early craftsmen used the cementation method.² Prior to the development of large-scale distillation of metallic zinc in the nineteenth century, this element was retrieved from calamine, a high-grade zinc carbonate ore.³ Furthermore, most of the unrefined copper ores, the so-called *Schwarzkupfer*, contained silver, which was extracted by means of a process called liquation. This technique, as described in Georgius Agricola's *De re Metallica*,⁴ relies on the insolubility of lead in copper at low temperature (see a typical lead inclusion in Figure 1). Lead is melted in the unrefined copper and dissolved in the silver, forming together a separate phase. The lead and silver are melted away from the copper by means of liquation, also called *Saigerung*. The liquation process however does not extract all the lead from the raw copper ore.

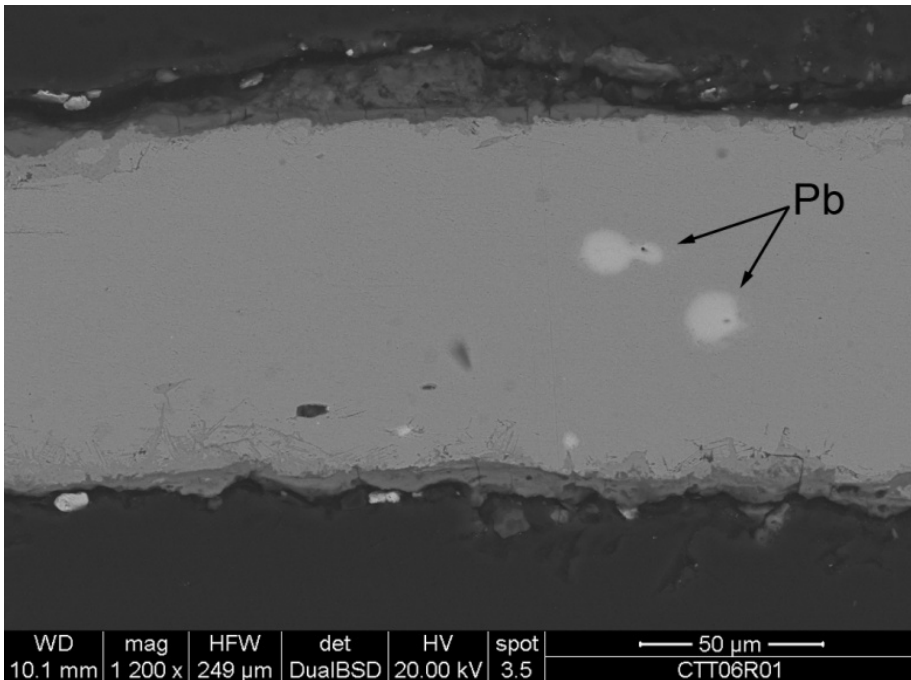


Figure 1: Scanning electron microscopic image of a cross-sectioned sample from a trumpet by Wolfgang Birckholtz (1650), showing some typical lead inclusions.

The presence of small amounts of lead improves the machinability of the alloy considerably. Today, lead in amounts up to 3% is added to certain brasses in order to improve their

cutting properties. However, the presence of lead in brass negatively affects certain crucial aspects of the brasswind construction process.⁵ It makes the alloy more brittle and increases the risk of stress-cracking; in other words, it negatively affects ductility, malleability, and cold deformation. The presence or absence of lead in the alloy is a particularly important issue in the construction of thin-walled brass instruments. The authors have observed walls as thin as 0.2 mm in early trombones. Therefore, from a musical instrument maker's point of view, one of the main parameters in the quality assessment of historical brass concerns the purity of the material (i.e., the absence of trace elements such as lead)—a consideration that is confirmed by a complaint made by several brasswind instrument makers of Markneukirchen in the eighteenth century.⁶

A sample of brass can be evaluated according to two principal variables: its microstructure and its chemical composition. The microscopic study of early metals is well-established.⁷ As a rule this type of study is destructive, because it usually requires cutting a sample, embedding it in resin, polishing the surface, and examining the result under magnification, such as with a scanning electron microscope (SEM). Such a procedure is inconsistent with internationally recognized standards of ethical treatment of early brasswind instruments.⁸ Furthermore, brass is subject to ageing, which involves a reaction of the material with substances such as sulfides and/or ammonia, making the material brittle. This process eventually results in stress-corrosion cracking. It is known, for example, that the hardness of brass can change over time, which makes analysis of old brass rather ambiguous if one aims to learn more about the material's original dynamic-mechanical properties.⁹

A great deal of work has been done on the chemical properties of metals.¹⁰ This work has been driven in particular by archeometallurgists, whose objective is to learn more about the provenance and authenticity of brass objects, based on the chemical elements present. Among the methods used for such evaluation, X-ray fluorescence (XRF), which is based on the analysis of secondary X-ray radiation by means of an energy-dispersive detector, is the most prevalent. This method is non-destructive, accurate, and portable, and it provides qualitative as well as quantitative results, which makes it particularly appropriate for the analysis of historic brass alloys; it has been used by several scholars of early brass alloys for this purpose.¹¹

The chemical analysis of historical brass is not without its problems, one of which is the inhomogeneity of the material, which can affect the accuracy of the results. The XRF method measures a particular surface area and gives a mean value from this spot. As can be seen in Figure 1, if there is a lead inclusion in this measuring field, a different end-value will be obtained, as compared to an area that has no lead. Therefore it is of great importance for the statistical value of the result to analyze as many different samples as possible.

Extensive research on the chemical composition of sixteenth-century brass objects has been done at the Rathgen Institute by Josef Rieder and his associates.¹² However, this research is concerned almost exclusively with cast objects. Brass was a rare and precious metal in the sixteenth century, and it is known that brass foundries recycled old brass and virtually re-melted together everything they considered to contain primarily copper

or zinc. Thus the chemical composition of cast objects cannot be compared to those made of sheet brass and wire.¹³ The study of Nuremberg sheet brass from the sixteenth century is dominated by the seminal work of Mitchiner, Mortimer, and Pollard on 273 Nuremberg jetons (*Rechenpfennige*).¹⁴ These jetons were found in the course of excavation work in the River Thames near London. Every jeton was cleaned of dirt and corrosion, and subsequently examined several times with XRF. The age of these jetons could be identified by means of production marks, covering the period 1475 to 1888.

Karl Hachenberg hypothesized that, in light of the Nuremberg trade laws,¹⁵ the material at the disposal of the Nuremberg jeton makers must have been the same material as that used by the early Nuremberg brasswind musical instrument makers. In 2006 he elaborated on the experimental data given by Mitchiner et al.¹⁶ Among these jetons, forty-two could be dated between 1550 and 1600, the period in which the musical instruments under consideration in this article were made. A descriptive statistical analysis resulted in a presumptive nominal value, indicated by the medians of approximately 18% zinc and 0.5% lead. Also, the trace elements tin (Sn), iron (Fe), nickel (Ni), silver (Ag), antimony (Sb), and arsenic (As) are present in the alloy. The values given in Table 2 indicate that sixteenth-century Nuremberg sheet brass had a high degree of purity and was thus of excellent quality. In order to verify Hachenberg's hypothesis, the next step was to compare the brass in the jetons with that in the sixteenth-century Nuremberg trombones.

	Zn	Pb	Sn	Fe	Ni	Ag	Sb	As
median	18.15%	0.55%	0.51%	0.19%	0.24%	0.08%	0.17%	0.22%
samples	42	42	42	23	41	40	25	15

Table 2: Median percentage of all chemical elements present in the alloys, with the number of samples.

Non-destructive analysis of the chemical composition of early brass with X-ray fluorescence

There are two main criteria for a method suitable for analyzing the chemical composition of historic brasswind instruments: it must be non-destructive and, ideally, portable. X-ray fluorescence (XRF) analysis meets both of these requirements.¹⁷ This technique is based on the process of photoelectric absorption:¹⁸ high-energy photons (the primary radiation) in the X-ray region of the electromagnetic spectrum are absorbed by the target atoms, thereby causing ionization of inner-shell electrons—that is, electrons are ejected (see Figure 2), creating vacancies in inner electron shells. The gap is filled by electrons falling from a higher energy level, losing their extra energy as X-rays. There are usually at least two peaks for each element. This is because of the energy transition that occurs. If there is one vacancy in the inner energy level, then there are a number of possible transitions to fill it. The target atom will return to a more stable electronic configuration in one of

two ways: in the form of an emitted photon or by transferring the energy to a second electron (a so-called Auger-electron). X-ray fluorescence operates by collecting counts from the detector, separating them according to their energy, and displaying the X-rays, generated as a spectrum.

The ratio between the number of these so-called characteristic or secondary X-rays and the number of Auger electrons emitted from the target atom is rather small for “light” elements (i.e., elements with a low atomic number). Hence XRF is especially well-suited for analysis of materials with a higher atomic number, such as the principal constituents of historical brass: Cu, Zn, and Pb. Quantitative information on the composition of the analyzed instrument can be obtained using the intensity (y-axis in the spectrum) of the corresponding X-ray lines (see Figure 3). Reference materials of known chemical composition and numerical algorithms, such as the fundamental parameter method, are used for this purpose.¹⁹

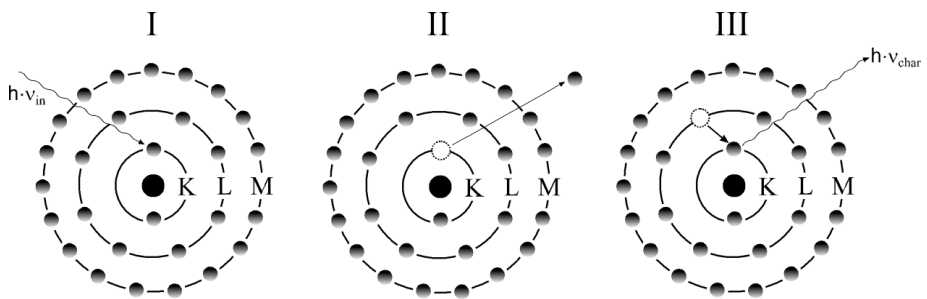


Figure 2: The principle of X-ray fluorescence analysis (XRF), beginning with the absorption of an incident photon (I), which causes a vacancy in an inner electron shell (II) and finally the emission of X-rays characteristic to the elements present in the investigated material (III).

The analysis presented here was carried out in the specific museums, utilizing the handheld X-ray spectrometer “xSort,” produced by Ametek-Spectro in Kleve, Germany (see Figure 4). This spectrometer is equipped with a silver target and a silicon drift chamber detector. The software “Leichte Elemente” was used to quantify the data. The analysis consists of two steps: first, a measurement with an accelerating voltage of 40 kV and a current of maximum 0.8 mA for six seconds; second, a measurement with an accelerating voltage of 15 kV and maximum 0.35 mA, with a collection time of thirty seconds. The spectrum of the first step is used to quantify the heavier elements, while that of the second is used for the lighter elements.

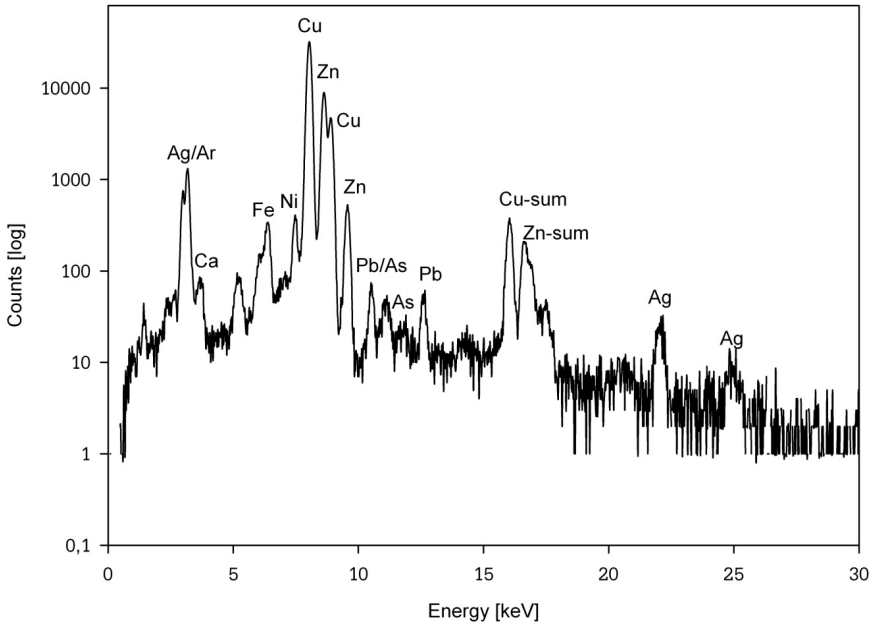


Figure 3: Example of a typical spectrum, showing the characteristic peaks of the elements copper (Cu), zinc (Zn), and lead (Pb).

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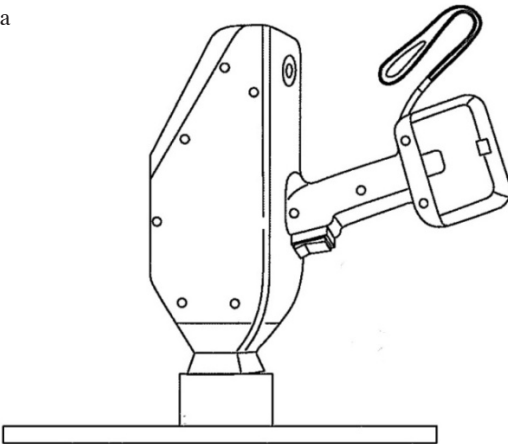


Figure 4: Experimental setup: (a) shows a schematic view of the instrument in measuring position; (b) illustrates the setup during measurement.

Influence of the corrosion layer on the accuracy of the results

In order to assess the accuracy of our method, it was essential to understand how the brown oxidation patina that covers several of the instruments might affect the quantification of the data. In order to investigate this, several samples, each 20 x 20 mm in size, were cut out of a sheet of standard CuZn15 (a copper alloy containing 15 percent zinc). The samples were coated with an artificial patina visually comparable to that found on the instruments, according to a recipe from Hughes and Rowe's book on the artificial patination of metals.²⁰ The samples were divided randomly into three groups and immersed in a boiling solution of 25 g ammonium carbonate, 12.5 g copper acetate, and 500 ml acetic acid (6% solution); these groups were immersed for four, five, and eight minutes respectively. Subsequently, these artificially patinated samples were measured with XRF and compared with one reference sample that was left uncoated. The data given in Table 3 indicate that increasing corrosion thickness results in a decrease in detected zinc content. The maximum difference between the untreated samples and those immersed for the longest period is about 1.5%. This is within the margin of error, which is in the order of magnitude of maximum 1.5–2%.

Sample	Element		
	Zn	Cu	Pb
<i>untreated</i>	13.60	86.00	0.12
4 min.	13.17	86.50	0.12
5 min.	12.70	86.93	0.13
8 min.	12.17	87.50	0.13

Table 3: XRF results obtained for brass samples, untreated and treated, in a mixture of ammonium carbonate, copper acetate, and acetic acid.

Findings

The frequency distribution of the zinc content in each of the measured points (653 in all) is shown in Figure 5. This histogram indicates that there are three main groups of data, clustered according to the amount of zinc present (Table 4). Group A contains the largest number of samples, 370 in all. These measurements are exclusively from component parts of instruments that can be identified as from the sixteenth century, and include tubes, bells, garlands, ferrules, and hinges. Group B can be divided into two sub-groups, the first consisting of replacement parts that are considered to have been made in the late seventeenth or eighteenth century; the second, of original ferrules that in spite of our expectations have the characteristic high zinc content associated with Group B. However, this second sub-group consists of only forty-seven samples, all from the four latest instruments in the study.²¹ It was possible to date approximately the component parts in Group C due

to the absence of soldering seams, an indication of manufacture after the middle of the nineteenth century.²² The chemical analysis of Group C component parts also reveals a characteristic pureness and homogeneity that one would expect of modern brass. Further, the surface conditions indicate that the material was rolled instead of hammered.

group	approx. date	Zn content in %	samples
A	<1600	15–22.9	370
B	<1600	23–28.9	47
	>1600	23–28.9	173
C	>1850	29–38.4	63

Table 4: The three main alloy groups found in the sixteenth-century trombones listed in Table 1.

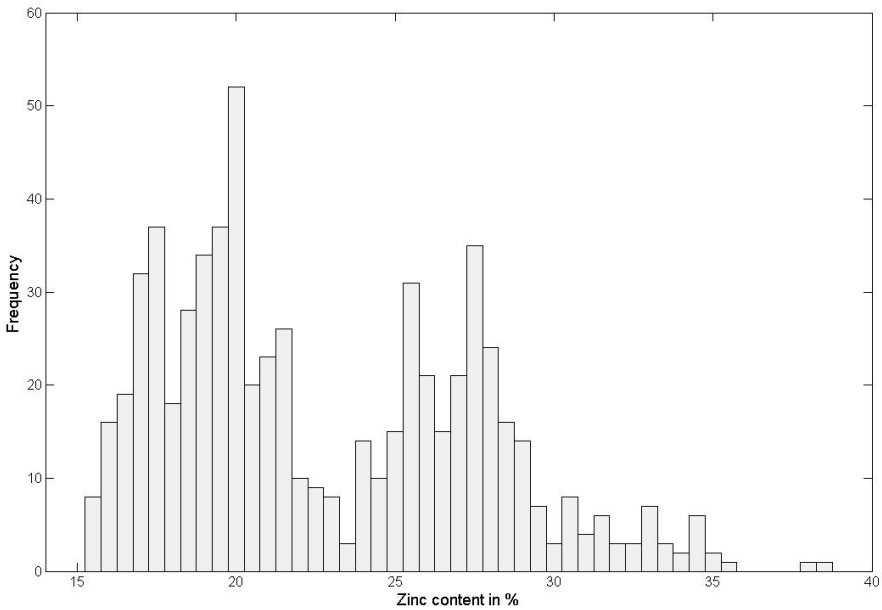


Figure 5: Frequency distribution of zinc content present in all measurements.

In addition to the clustering of the data in three groups, mentioned above, Figure 5 also shows the rather wide dispersion of the data. In order to obtain a representative value for each element from such diverse groups, statistical analysis was needed. The common measures of central tendency are given in Tables 5 and 6. All values from this analysis are also depicted in the Appendix in scatter plots. Fifteen measured points have been

	Zn	Cu	Pb	Sn	Al	Fe	Ni	P	Si	As
mean	19.01	76.83	1.02	0.19	1.20	0.20	0.19	0.15	0.88	0.21
first quartile	17.50	75.70	0.63	0.08	0.78	0.12	0.08	0.06	0.19	0.10
<i>median</i>	19.10	77.30	0.88	0.09	1.04	0.18	0.15	0.11	0.47	0.16
third quartile	20.20	78.80	1.23	0.34	1.46	0.25	0.30	0.18	1.14	0.26
mode	18.80	79.00	0.73	0.09	1.15	0.16	0.01	0.06	0.05	0.15
stand. deviation	1.74	3.06	0.58	0.18	0.70	0.12	0.14	0.12	0.97	0.13
<i>samples</i>	355	355	355	231	338	323	282	141	253	101

Table 5: Analysis of central tendency of Group A test areas in %.

	Zn	Cu	Pb	Sn	Al	Fe	Ni	P	Si
mean	27.64	66.15	1.42	0.55	1.49	0.24	0.09	0.10	2.61
first quartile	27.38	63.45	1.10	0.10	0.92	0.16	0.06	0.07	0.48
<i>median</i>	27.70	67.57	1.36	0.52	1.44	0.21	0.08	0.09	1.46
third quartile	28.25	68.20	1.51	0.72	2.20	0.37	0.11	0.12	4.88
mode	27.70	67.90	1.55	0.08	2.26	0.23	0.08	0.09	0.25
stand. deviation	1.25	3.70	0.65	0.53	0.75	0.12	0.07	0.05	2.51
<i>samples</i>	47	47	47	45	47	43	40	29	38

Table 6: Analysis of central tendency of Group B test areas in %.

excluded from analysis, because they clearly were statistical outliers caused by errors in measurement.

Discussion

Consistent with the recent work of Karl Hachenberg,²³ the results in Tables 5 and 6 indicate that an alloy of approximately 19% zinc and 0.9 % lead content can be found in sixteenth-century brasswind instrument parts. Therefore such an alloy could be said to be characteristic of sixteenth-century Nuremberg brass, and could be considered appropriate for the purpose of manufacturing reproductions of Nuremberg instruments from this period. In total, 402 measurements were collected from component parts that can be dated to the sixteenth century. Among these, forty-seven measurements indicate significantly higher zinc content, similar to component parts that were manufactured later. However, these measurements were identified only in a limited number of ferrules, which are not considered to be acoustically effective parts of a trombone.

Archeometallurgists have carried out a great deal of work on trace elements found in historical brasses in an effort to learn more about an artifact's provenance through its original ore.²⁴ This area of research, however, is to some extent problematic, and it has generated controversy in some instances.²⁵ Discrepancies can be seen, for example, between the trace-element composition of the natural ore and that in the finished item, due to the production process. Furthermore, the inhomogeneity and corroded/patinated surface conditions of the material could affect the capture and analysis of representative chemical data. In the course of this research, it has also been seen that the ratios relating

to accelerating voltages, current, and measuring time play a decisive role in the accuracy of the capturing process. In light of these difficulties, the small values of trace elements shown in Tables 5 and 6 should be considered with caution.

Concerning the trace elements, the fact that aluminum was detected was rather surprising, since several scholars regard the presence of aluminum in historic brass as a decisive argument for dating such objects to the late eighteenth or even nineteenth century. However, upon close examination of the raw data, it was clear that the measuring equipment unequivocally registered aluminum. In order to gain insight into the presence of aluminum in musical instrument component parts that are attributed to the sixteenth century, a small specimen of a Nuremberg trumpet made by Wolf Birckholtz in 1650 was mounted in resin, polished, and analyzed with a scanning electron microscope (SEM/EDX). The resulting X-ray mapping of a cross section of the corrosion layer (see Figure 6) shows that the aluminum was detected only in the surface layer; it is not present in the original bulk material. The aluminum, however, was detected with the elements calcium and silica, and it is likely that the aluminum, calcium, and silica are derived either from dust or a cleaning product.

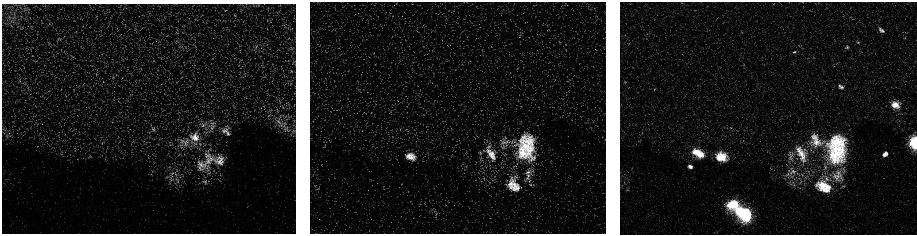


Figure 6: X-ray mapping of a sample of a seventeenth-century Nuremberg trumpet by Wolfgang Birckholtz, showing the presence of aluminum (center) in combination with calcium (left) and silica (right).

The difference in physical properties between a contemporary brass alloy (commonly 63:37 Cu:Zn) with a significantly higher zinc content than the characteristic historic alloy described in this article (80:19 Cu:Zn with 0.9% Pb) is considerable, and it has a direct effect on structural vibrations.²⁶ In recent years, advanced numerical techniques have been widely adopted in the study of structural vibrations and in particular in the study of the influence of material composition on wall vibration in brasswind instruments. The search for an answer to this question was of particular concern to leading musical

instrument makers as early as the nineteenth century.²⁷ In spite of intensive research and considerable progress in this field,²⁸ one of the most persistent questions still remains: what is the significance for historically informed performance of the use of a historically correct alloy in reproductions of brasswind musical instruments?

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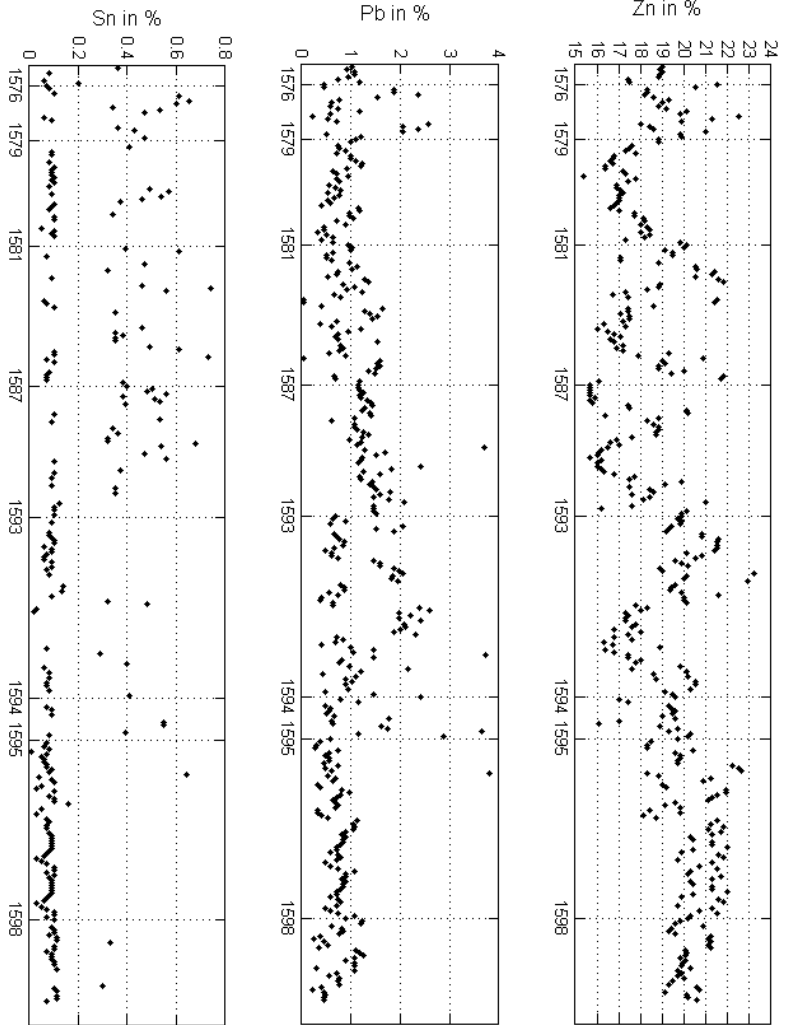
Manfred Schreiner is Head of the Institute of Natural Science at the Academy of Fine Arts, Vienna. He was rewarded a second Ph.D. (Habilitation) in analytical chemistry in art on the application of surface analytical techniques by studying the deterioration process of medieval stained glass. His work has focused in particular on the analysis of cultural artifacts with state-of-the-art diagnostic equipment.

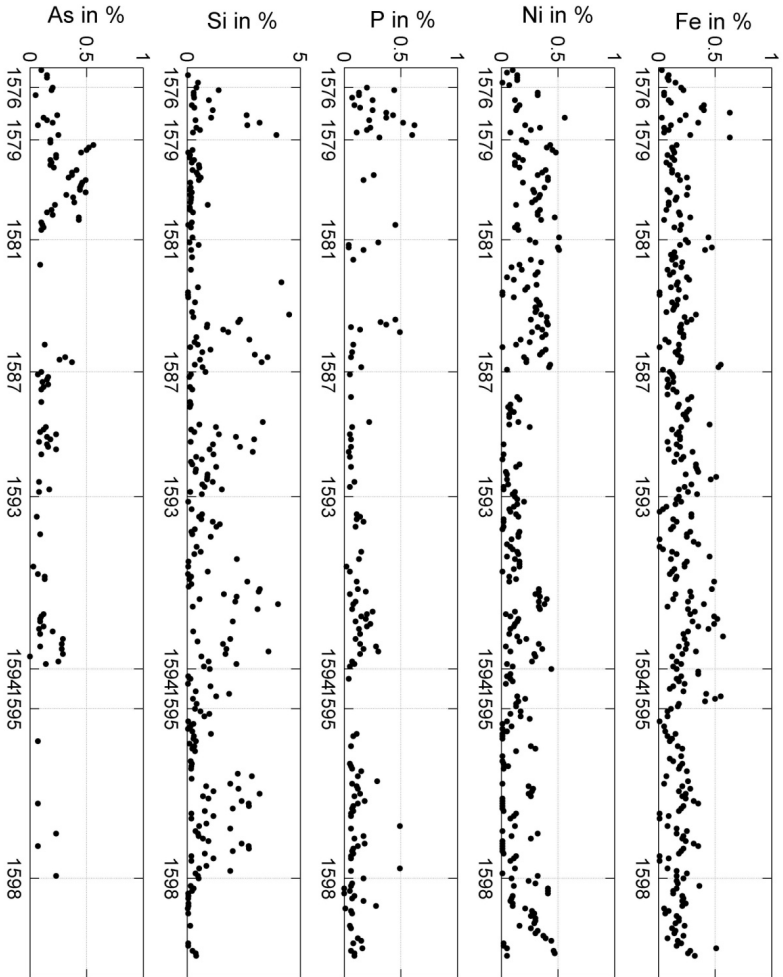
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APPENDIX

Chemical composition of sixteenth-century trombone components





NOTES

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² David Bourgarit and Fanny Bauchau, "The Ancient Brass Cementation Processes Revisited by Extensive Experimental Simulation," *Journal of the Minerals, Metals and Materials Society* 62/3 (2010): 27–33.

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⁴ Georgius Agricola, *De re metallica libri XII* (Basel: Johannes Froben, 1556).

⁵ Karl F. Hachenberg, "Brass in Central European Instrument-making from the 16th through the 18th Centuries," *Historic Brass Society Journal* 4 (1992): 229–52, here 240.

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⁸ Robert Barclay, "Ethics in the Conservation and Restoration of Early Brass Instruments," *Historic Brass Society Journal* 3 (1991): 75–81.

⁹ Dies, *Kupfer und Kupfer-Zink Legierungen*, 322.

¹⁰ Mark Pollard and Carl Heron, *Archaeological Chemistry* (Cambridge: The Royal Society of Chemistry, 2008).

¹¹ Louise Bacon, "A Technical Study of the Alloy Compositions of 'Brass' Wind Musical Instruments (1651–1867) Utilizing Non-Destructive X-Ray Fluorescence" (London: thesis submitted to the Institute of Archaeology, University College, 2003).

¹² See, for example, Josef Riederer, "Die Bestimmung der Herkunft von Teilen von Messingleuchtern des 16. Jahrhunderts aus einem Schiffsfund," *Mitteilungen des Vereins für Geschichte der Stadt Nürnberg* 78 (1991): 265–67.

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¹⁴ Michael B. Mitchiner, Catherine Mortimer, and Mark Pollard, "Nuremberg and its Jetons, c. 1475 to 1888: chemical compositions of the alloys," *Numismatic Chronicle* 147 (1987): 114–55.

¹⁵ See: August Jegel, *Alt-Nürnberger Handwerksrecht und seine Beziehungen zu anderen* (Neustadt an der Aisch: C.W. Schmidt, 1965).

¹⁶ Hachenberg, "Der Werkstoff Messing," 433–48.

¹⁷ Koen Janssens, "Use of Microscopic XRF for Non-destructive Analysis in Art and Archaeometry," *X-Ray Spectrometry* 29/1 (2000): 73–91.

¹⁸ Koen Janssens and René van Grieken, *Non-Destructive Microanalysis of Cultural Heritage Materials* (Amsterdam: Elsevier, 2004), 129–226; Rudolf O. Müller, *Spektrochemische Analysen mit Röntgenfluoreszenz* (München: Oldenbourg, 1967).

¹⁹ Gerard R. Lachance and Fernand Claisse, *Quantitative X-ray Fluorescence Analysis, Theory and Applications* (Chichester: John Wiley & Sons Ltd., 1995).

²⁰ Richard Hughes and Michael Rowe, *The Colouring, Bronzing and Patination of Metals* (New York, Watson-Guption Publications, 1991), 287.

²¹ While some ferrules on these instruments have a higher "Group B" zinc content, others on the

same instrument could be associated with the low zinc alloy characteristic of Group A. Obviously the brass used in the late-sixteenth-century ferrules, which are acoustically ineffective, was chosen more or less randomly.

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²⁴ Mark Pollard and Carl Heron, *Archaeological Chemistry*, 222.

²⁵ *Ibid.*, 303.

²⁶ Vasileos Chatziioannou, Wilfried Kausel, and Thomas Moore, "The Effect of Wall Vibrations on the Air Column Inside Trumpet Bells," in *Proceedings of the Acoustics 2012 Nantes Conference* (Nantes, France), 2243–48.

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