ANALYSIS OF HEAVY METALS IN SMOKE DEPOSITS IN THE LIMEWASH OF THE ROYAL ARTILLERY FACTORY OF SEVILLE (17TH CENTURY): CONTRIBUTIONS TO THE LOCATION OF THE FURNACES*

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The Royal Artillery Factory of Seville in Spain originated from pre-existing private bronze foundries dating from the 16th century. The paper analyses the stratigraphy of wall cladding in the areas traditionally known as the 'Old Foundry' and the 'New Foundry', through its characterization by optical microscopy, scanning electron microscopy with energydispersive X-ray spectrometry (SEM-EDX), micro-X-ray fluorescence (μ -XRF) and micro-Xray diffraction (μ -XRD), in order to analyse the metal deposits that have accumulated since the 17th century. The data obtained allowed the verification of the available historiographical information and the location of the original bronze smelting furnaces. The analysis of patinas deposited on the overlapping layers of lime also confirmed that neither the raw materials nor the composition of the alloys used presented any substantial changes.

KEYWORDS: PATINAS, CASTING, HEAVY METALS, BRONZE, THE ROYAL ARTILLERY FACTORY OF SEVILLE, LIMEWASH

INTRODUCTION

The Royal Artillery Factory of Seville (RAFS) was one of the main exponents of the regeneration of Spanish industry, inspired by Jean-Baptiste Colbert's model based on the creation of a powerful industry driven by the state and independently of guilds (Souto Rodríguez 2004). It is also the best-preserved example. The RAFS has its origin in the bronze foundries built in the San Bernardo district of Seville in the 16th century. The most important foundry—the Bronze Factory of Seville (1565)—was run by Bartolomé Morel. Apart from metal production, this first foundry supplied artillery to vessels in the Indies Fleet (Aguilar Escobar 2008). Although archives contain abundant documentation on this building (Roig del Negro 2001), providing comprehensive historiographical information, successive historical studies have so far not been complemented with archaeological analyses. While the information available on the addition of the foundries, which were later acquired by the Treasury in 1634 for their administration under an administrative concession until 1717 (Carrasco y Saiz del Campo 1887), is confusing, the subsequent evolution of the building has not been researched in full, with the existence, contrary to tradition, of an 'Old Foundry' (OF) and a 'New Foundry' (NF). The formal analysis, based on the study of

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documentation and conserved architectural structures, suggests that no remains have been conserved from the period before the projects undertaken by Juan Navarro in 1720 and Ignacio Sala in 1730 (Roig del Negro 2001). All the documentation related to the different projects of the building and the corresponding plans can be found in the Simancas General Archive (Valladolid, Spain); this archive preserves all the documentation produced by the governing bodies of the Spanish monarchy between 1475 and 1834.

Carlos III, King of Spain (r. 1759–88), promoted the construction of a new factory imitating the great French royal foundries. After numerous difficulties, the project presented by the Flemish engineer Jorge Próspero Verboom was chosen for the construction of completely new installations (Rabanal Yus 1990). As a result of growing production needs, the project underwent numerous modifications, culminating in a majestic building that was eventually completed in 1796 under the reign of Carlos IV (Mora Piris 1994). Historical records confirm that the Swiss military engineer Jean Maritz designed the building in 1767 (Ollero 2015, 215). The NF, which was integrated into an existing construction, the new building designed by Navarro in 1720, was continued by Sala in 1731 following the acquisition of an adjoining property on the south side (Carrasco y Saiz del Campo 1887).

This NF, together with the constructions inherited from the 17th century, may have been that referred to as the OF in preserved documentation V (Roig del Negro 2001). The extension project undertaken in 1759 was supervised by the artillery commander Juan Manuel de Porres, the foundry's director, together with the architect Pedro de San Martín, who was chief municipal architect from 1749 until his death in 1784 (Ollero 2012, 27), and who imbued the foundry with his peculiar style. Although initial work on this building was strongly criticized in 1763 for its poor execution (Roig del Negro 2001), it clearly set the architectural road map for the new factory, attributed by all historians to the smelter Maritz.

Although the NF was initially conceived as a standalone project, and despite criticism of the completed construction work by Porres's successor at the helm of the institution, everything suggests that nothing built from 1731 was demolished and that, in contrast, all new construction work came under the scope of the new extension project.

The new factory came to house three blast furnaces and six smaller ones for the foundries, as well as the necessary installations for refining metals, with five reverberatory furnaces and two cupels, warehouses for storing raw materials, moulds and manufactured products, at least two mills, one animal powered with stables for thirty horses, administrative offices and various ancillary workshops, such as those dedicated to drilling, chiselling, refractory brick-making and carpentry (de la Vega Viguera 1992; Aguilar Escobar 2008).

As a result of the evolution described above, the constructive analysis of the RAFS is imprecise due to the series of buildings and industrial facilities erected and superimposed simultaneously to satisfy the production demands of the expanding empire and technological developments at the time. The analysis of historiography indicates that an OF, the result of the successive projects undertaken by Salas, Verboom, Navarro and Porres, coexisted in the current building with another NF, the work of Maritz, on the assumption that the initial 16th- and 17thcentury installations remained operative (Rabanal Yus 1990; Aguilar Escobar 2008; Sobrino Simal 2011, 89). It seems logical that both facilities would have coexisted once the NF came into operation, although it is unclear whether the OF underwent any modifications. It is conceivable that the investment in these spaces was amortized through new uses, adapted by virtue of architectural reformation work.

This archaeometric research was based on the abovementioned reflections and confirmation of the existence of smoke deposit sequences covered by layers of limewash, taking into consideration the information provided by the patinas of smoke conserved below the layers of paint. There are studies on heavy metal deposits and their migration from smelting slag in which one can find similarities in their stratification, despite having a different behaviour with respect to the metals of the smelting fumes. According to Maskall *et al.* (1995), the extent and rate of metal migration are influenced by the nature of the matrix of the material over which it is deposited. There are also studies of deposits due to the high concentrations of heavy metals in the environment, as in the research on animal bones in a mediaeval copper workshop (Grattan *et al.* 2005; Müller *et al.* 2011). There are also studies on vegetation as a support for deposits; it also may accumulate heavy metals as copper and lead from metalliferous smelting activity (Pyatt *et al.* 2000).

As an eminently industrial construction, it seems evident that the materials deposited on the walls, as a result of activities performed in the installations over the centuries, serve as a document of the building's history (Rubio-Bellido *et al.* 2012). The formation of an alternate superposition of patinas composed of foundry fumes and casting and limed layers has given rise to a temporal sequence that reflects the metallurgical work carried out there (Barbero-Barrera *et al.* 2014, 326; Baxter *et al.* 2016, 1218). The oldest preserved documentation about the smelting activity carried out in the RAFS contains records that around 900 T/year of copper and tin were smelted there in the mid-17th century, giving an idea of the volume of material processed in the factory (Aguilar Escobar 2008).

The objectives of this study were as follows:

- To determine the presence of heavy metals and their identification in the smoke deposits on the layers of paint in order to confirm that they originate from the furnaces in the areas defined as OF and NF.
- To evaluate similarities and differences between the different finishing layers comprising the coating, which can provide information on possible changes in the composition of the alloys manufactured over time.
- To determine whether the storage areas where the OF is purported to have been located coincide those that have been preserved until the present or if they disappeared during any of the reforms carried out in the industrial complex of the RAFS. The successive paint layers applied to the walls would have concealed any deposits; hence, the stratigraphic series would correspond to a historical record or sequence.

SAMPLING CRITERIA, LOCATION AND PROCEDURE

The studies carried out on the building were used as a reference to identify the areas where the most relevant industrial activity may have been concentrated, resulting in the identification of the aforementioned areas designated as OF and NF. From this division, superior elements, such as domes and vaults, were treated as sampling points, as these would have been the areas with the highest concentrations of smoke and, consequently, the locations of metal deposits that could provide more information about casting, in order to verify the historiographical information and document the activity developed in the aforementioned areas (Flores-Alés *et al.* 2017, 83).

The samples analysed originated from coating in the areas identified as OF and NF, comprising stratigraphic sequences with a variable number of alternating layers of paint and patinas of smoke deposits. Sampling in the area designated as NF was carried out in the dome, as a smoke outlet area of the first smelter (Fig. 1). In the area referred to as OF, samples were taken in the intrados of the arches, above the impost, according to the interpretation of the original location of the furnaces in Verboom's project (Fig. 2).

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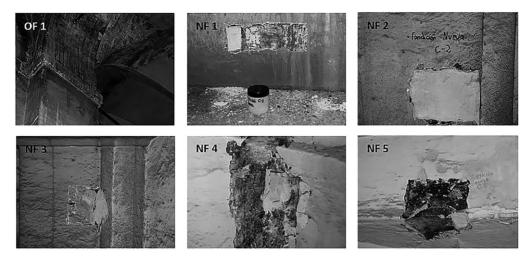


Figure 1 Sampling at the Old Foundry (OF1) and the New Foundry (NF1-5).

The extracted materials correspond to five samples from the NF (NF1-5) and three from the OF (OF1-3) (Fig. 3). Although the damage caused was not particularly severe, we limited the extraction and extension of the samples as much as possible, attempting to take advantage of areas that had been surveyed previously (Singh et al. 2015, 156). The samples were extracted by deep cutting with a scalpel in order to obtain the complete set of layers. This procedure was particularly complex due to the separation between layers caused by their fragility and the uneven state of the aggregation coating (Fig. 3). The intense activity developed in the RAFS from the moment it came into operation is revealed by the fact that in some areas where the sampling was carried out, the first black smoke deposits appeared directly on the plaster of the wall, indicating that casting activity started from the moment the building entered into service, without the typical liming present in other areas. The observation during the sampling collection of a first smoke deposit on the lime plaster of the wall (OF) and several layers of deposits alternated with layers of the NF (Fig. 3), allows the idea that no cleaning operations have been carried out on the walls to be established as a reliable hypothesis. This is supported by the size of the building, the height of the domes and that the maintenance has been limited over time to cover the dirt of smoke with layers of lime paint, as confirmed in the stratigraphic study (Fig. 4). It is important to highlight that in samples taken in the OF area, only one blackened film was identified, while in the NF all the samples presented several strata.

METHODS

In order to carry out a preliminary study and describe the stratigraphic sequences, samples were embedded in methacrylate resin and then cut with a diamond disk. Finally, the sections were finished by means of polishing with a rotating disk when wet (Jiménez-Roca *et al.* 2005, 382). The samples were viewed under a LEICA model S8 APO stereo zoom microscope, with a LEICA DC300 capture camera and IM50 (Image Manager) software v.1.20, in order to analyse the structure of any layers that covered the walls and their thicknesses (Blasco-López *et al.* 2015, 463).

The sample characterization process was continued with the identification of the mineralogical nature of the different layers of paint, corresponding—as their appearance reveals—to layers of

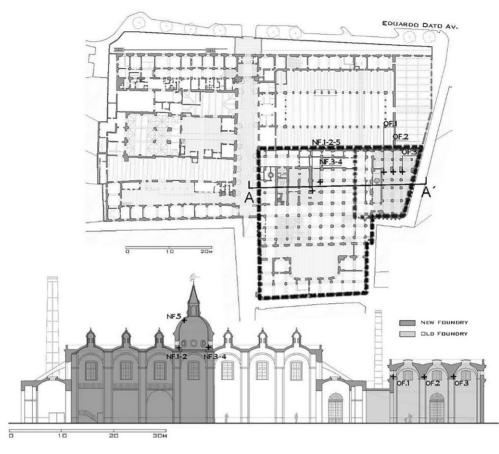


Figure 2 Layouts and elevation of the Royal Artillery Factory of Seville (RAFS) with the area corresponding to the New Foundry (NF) highlighted in pink (samples NF1–5) and the Old Foundry (OF) in yellow (samples OF1–3). The layout is currently preserved from the 1725 and 1759 projects.

liming. Given the difficulty in identifying the mineralogy in thin layers, micro-X-ray diffraction (μ -XRD) was used with a Bruker D8 Discover diffractometer equipped with a copper anode, focusing optics and X-ray polycapillary system, which allowed the mineralogical composition of a small section of the sample with areas up to 50 µm in diameter to be determined (Berthold *et al.* 2009, 107).

The heavy metal elements in the smoke deposits forming the stratigraphy were initially identified by spot chemical analysis with μ -X-ray fluorescence. An EDX Eagle III model was used, equipped with Low Mag 10× (colour) and High Mag charge-coupled display (CCD) 100× (colour), enabling the qualitative and quantitative analysis of the detected elements (Bindler and Rydberg 2016, 642). The results obtained were limited to an area of 300 μ m in diameter, which tended to overlap two to three layers in the stratigraphic sequence and greatly exceeded the size of any heavy metal particles that may have been deposited. For this reason, they were contrasted by scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDX) analysis under a Phillips XL-30 microscope. The samples were metallized beforehand with gold sputtering, thus improving the resolution and the ability to search for particles with heavy metals

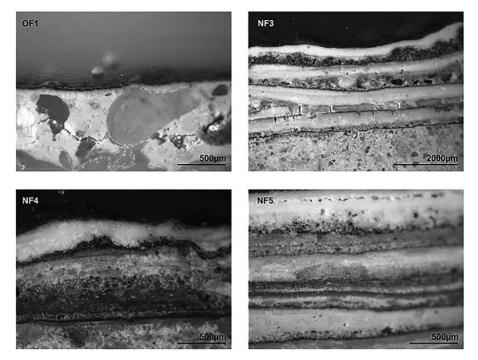


Figure 3 Stratigraphy of sample OF1 ($63\times$) with a single smoke layer and NF3 ($20\times$), NF4 ($63\times$) and NF5 ($63\times$) with several alternating smoke and paint layers.

within each stratum in back-scattered electrons (BSE) mode and their chemical analysis, thus minimizing the presence of the matrix in which they were embedded (Maravelaki-Kalaitzaki 2005, 187).

DISCUSSION

Study of the stratigraphic structure

Optical microscopy analysis was carried out to obtain an initial description of the sample sections and thus be able to measure, identify and record the sequence of paint layers and smoke/deposits. Image analysis also allowed the aggregation status of the strata and their degree of adhesion to be verified, which was interesting because we were able to observe the fragility of the layer and the ease with which they fractured.

A characteristic feature observed in the samples from the OF (OF1–3) was a single, thin, black layer, normally $< 20 \,\mu$ m. This layer was deposited directly onto the lime plaster layer forming the original coating because the stratigraphy did not reveal a previous paint layer applied as preparation for the support (Fig. 3, OF1).

The samples taken in the NF presented significantly different stratigraphic sequences to those in the OF, although a certain similarity was observed between them (Fig. 3, NF3–5). Samples NF4–5 had up to four grey layers, alternating with the corresponding paint layers, and were clearly diffused in some cases due to dragging on the upper paint layer. They could be associated with the smoke deposits and not all presented the same state of aggregation, although cohesion

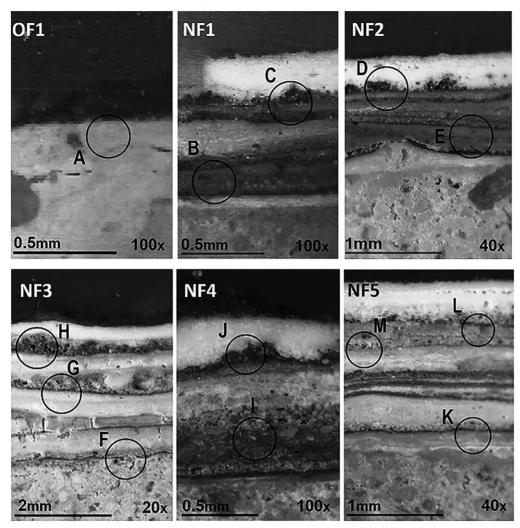


Figure 4 images of OF1 and NF1–5 indicating the areas analysed and their designation.

was generally poor. Samples NF1–3 presented a similar structure, the difference being that two coats of paint seemed to have been applied in some layers; in these samples, the diffusion of the smoke particles was not as evident as in sample NF5. In the case of sample NF2, the abundance of strata and their thinness made them difficult to define. We were therefore unable to estimate the nature of the individual strata. Noteworthy characteristics included the greater cohesion and apparent hardness of the paint layers, initially identified as limewash, compared with the less cohesive smoke layers.

Observation of the samples from both foundries confirmed that in all cases the first smoke layers were deposited directly onto the mortar lining. There were no signs of any previous paint layers. In a building of these dimensions, the foregoing could have been due to the successive reforms undertaken during the 17th century in the RAFS, resulting in the walls being finished with a single layer of plaster, as well as the industrial activity carried out therein. The

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stratigraphic layers in the NF generally comprised a final paint layer, which, according to the logical chronological sequence, would have been plastic paint (polymeric resin) due to its texture and flexibility.

Optical microscopy also allowed the texture of the mortars used in the wall plastering to be studied (Miriello *et al.* 2011, 794). A clear difference was observed between the materials used in both foundries, revealing complete differences in the types of aggregate, colour, appearance and texture of the binder. The lining mortars of the OF were light cream in colour and comprised thicker sands (a maximum size of 0.55 mm), with the appearance of discontinuous granulometry, whereas the samples from the NF were brown in colour and presented homogeneously distributed aggregate granulometry with a maximum size of < 0.21 mm (Fig. 3).

Micro-X-ray diffraction (µ-XRD)

As regards the results of the μ -XRD analysis of the paint layers in the NF, all the layers and samples presented a similar mineralogy; gypsum was the majority mineral, calcite ($CaCO_3$) was present in lower quantities and traces of quartz (SiO_2) were observed. Although this composition could have been indicative of the use of a plaster-based paint with limestone and quartz impurities, such paint was not normally used in Seville during 16th-17th centuries (Mercado Hervás 1992; Robador González 2000). It is more reasonable to assume that these were liming or whitewash paints, in which $CaCO_3$ originated from the carbonation of calcium hydroxide (Ca(OH)₂) with atmospheric carbon dioxide (CO_2) . Later, due to environmental contamination caused by the presence of sulphur dioxide (SO₂) originating from either sulphur impurities in American cooper (Roig del Negro 2001) or coal-fired furnace combustion gases, fuel containing fractions of organic sulphur that produced SO₂ when oxidized at high temperatures (Suárez-Ruiz et al. 2006, 171; Wagner and Álvarez 2010, 239), partial sulfation of the CaCO₃ occurred, catalyzed by the presence of particulate carbonaceous matter (Novakov et al. 1974; Fuzzi and Vittori 1975, 19; del Monte et al. 1981, 645) and accelerated by the presence of certain transition and other metals (Fe, V, Cr, Ni, Pb, etc.). These metals catalyzed SO₂ hydrolysis and oxidation to form sulphuric acid, which was responsible for sulfation (Urone et al. 1968, 211). The stages of this process (SO₂ oxidation, hydrolysis and acid attack) took place according to the following reactions (Fassina 1988, 317; Rodriguez-Navarro and Sebastián 1996,79):

$$\begin{split} &2SO_2+O_2{\rightarrow}2SO_3\\ &SO_3+H_2O{\rightarrow}H_2SO_4\\ &H_2SO_4+CaCO_3+H_2O{\rightarrow}CaSO_4 \end{split}$$

Micro-X-ray fluorescence (µ-XRF)

The chemical analysis by μ -XRF (Table 1) confirmed the initial hypothesis: heavy metal elements were present in all the samples analysed in the NF and in the different strata of each sample (Fig. 4).

 μ -XRF analysis of the NF samples revealed that calcium oxide (CaO) and sulphuric oxide (SO₃) were the major elements in all of them, present in the limewash that originally covered the walls and whose detection was predictable considering the results obtained by μ -XRD. SO₃ was highly variable depending on the sample and area analysed, and depended on the exposure times of each liming layer to the fumes from the furnaces that caused the sulfation of the calcite before new layers were applied.

Table 1 Chemical composition of areas A-K by micro-X-ray fluorescence (μ -XRF) in OF1 and NF1-5

	$W_{t} q_{0}$												
Oxide	Oxide OFI NF1	NFI		NF2		NF3			NF4		NF5		
CaO	A	В	С	D	Е	Ч	G	Н	Ι	J	K	L	Μ
SO_3	57.44	40.44	65.37	38.50	64.94	77.85	48.31	39.49	35.43	59.91	79.78	38.44	47.94
SiO_2	2.95	54.61	28.66	56.22	28.25	17.84	43.96	51.30	58.85	27.86	15.44	56.06	34.72
Al_2O_3	36.56	2.96	2.67	3.19	4.01	1.87	5.13	4.49	3.13	5.67	1.66	2.48	3.78
K_2O	I	0.86	1.07	0.96	0.66	0.71	0.91	1.35	1.24	I	0.62	1.51	1.20
Fe_2O_3	1.74	0.58	0.49	0.58	0.50	1.34	0.48	0.65	0.55	1.15	1.77	0.82	1.13
CuO	1.08	0.33	1.65	0.34	1.56	0.30	1.11	2.58	0.63	5.10	0.24	0.55	10.66
ZnO	I	0.10	0.09	0.08	0.08	0.04	0.05	0.05	0.05	0.07	0.21	0.07	0.14
SrO	I	I	I	I	I	0.04	0.05	0.06	0.04	0.19	0.15	0.07	0.17
Ni_2O_3	0.09	0.03	I	0.06	I	I	Ι	0.02	0.04	0.06	0.07	I	I
PbO_2	I	I	I	I	I				I	I	0.07	I	0.27
TiO_2	I	0.09	Ι	0.07	Ι				0.05	I	I	I	I
	0.13	I	I	I	I				I	I	I	I	I

Heavy metals in smoke deposits of the Royal Artillery Factory, Seville

Interestingly, heavy metal elements were identified in the different samples and areas in the NF, notably traces of copper (Cu) and zinc (Zn), common components in bronzes, which always accounted for > 85% of the alloys used (Aguilar Escobar 2008). The different percentages of Cu and Zn analysed in the selected areas B–K (NF1 and 3–5) (table 2) are due to the intra- or interstratum heterogeneity, highlighting the fact that a behavioural pattern or fractionation in the heavy metals of the deposits does not exist. Other elements were also observed whose presence in traces may be associated with possible impurities in the raw material, such as aluminium (Al), lead (Pb) and nickel (Ni). It was striking that tin (Sn)—a metal that is part of bronze—was not detected by μ -XRF. However, SEM-EDX microscopy clearly confirmed its presence in the samples studied. One metallic element that appeared as a minority in the samples was iron (Fe), its presence in smoke deposits probably being due to the entrainment of iron oxide particles with the fumes of the furnaces, originating from coal ash (Suárez-Ruiz *et al.* 2006, 171; Wagner and Álvarez 2010, 239), or the incorporation of iron oxide pigments in the lime paint used on the walls; not all the layers of the images taken with optical microscopy were white but some presented yellowish tones.

The results of the analysis of deposits obtained from the OF were significantly different to those obtained for the NF samples. The major basic components of sample OF1 were CaO and silica (SiO_2) , which are due to lime plaster, while SO₃ content was much lower than in the NF samples and the different heavy metal elements (Cu, Zn, Pb) were not detected. If they had been present in the environment, they should have been fixed in an analogous way in both supports (lime plaster OF and limewash NF), because both were constituted mainly by a calcareous matrix (CaCO₃) from the carbonation of the lime Ca(OH)₂ either as mortar binder or as painting.

Considering that the presence of SO₃ in the different liming layers originated from sulfation with the combustion gases from the coal-fired furnace and the absence of heavy metals, it may be assumed that independently of any suppositions based on local historiographical sources, the furnaces were not located in the preserved construction elements of the OF and the activity carried out therein must have been different from the smelting operations. These results suggest that the deposit of $< 20 \,\mu\text{m}$ detected in OF1–3 (Figs 3 and 4) was possibly a layer formed by the accumulation of dirt, and whose current appearance resembles the smoke deposits in the area designed by Maritz.

SEM-EDX

The images obtained in BSE mode enabled the correct identification of the heavy metal particles in the whole image, since they generally presented a background of grey colours in the different layers due to the composition of mainly light chemical elements (Si, O, C, Ca, S, Al and Mg) while the particles that contained elements of high atomic weight stood out because they were clearly white and dispersed between the layers of lime that contained the smoke deposits (Figs 5, A–F).

This observation confirmed the interpretation of the results obtained with μ -XRF, namely the absence of heavy metal particles in any of the OF samples (OF1–3), the majority components being silicon (Si), calcium (Ca) and carbon (C), basic elements of the coating mortar. In contrast, in the NF zone, a carbon matrix from unburned remains was observed between the lime layers, where the heavy metal particles from the smoke deposits from the bronze foundry were dispersed (Figs 5, A–F). The diameters of these particles ranged between 12 and 50 μ m, without significant differences being detected between the different samples.

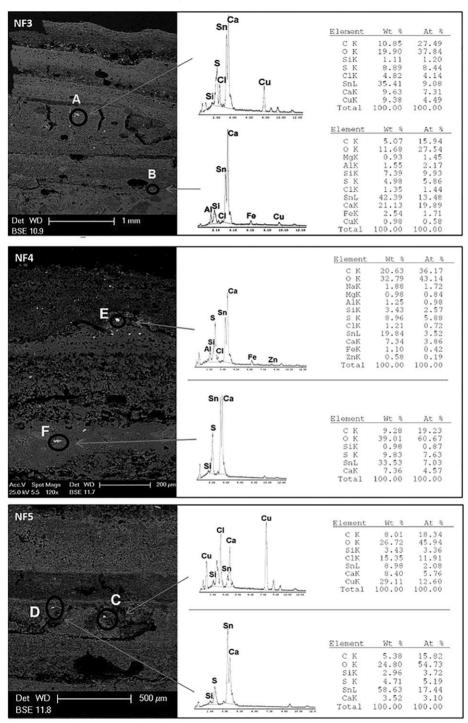


Figure 5 Micrographs of samples NF3–5 detailing the heavy metal particles analysed and the chemical composition spectra obtained.

Evidently, Cu, Sn and, to a lesser extent, Zn were the heavy metal elements identified in the samples from the analysis of the white particles observed in the SEM BSE microscopy images. The study of the composition of these metals revealed two types of particles: those composed mainly of Sn (Figs 5, B and D–F); and those composed of Cu and Sn (Figs 5, A and C)—in the case of the former, given the formation of gypsum as a result of the association of S with Ca, the lack of shared atomic stoichiometric proportionality between these elements and the identification of Ca as CaCO₃. It is also reasonable to assume that Sn was mainly present in oxide form, specifically tin dioxide (SnO₂), since tin(II) oxide (SnO) is a metastable compound that disproportionates as metallic tin and SnO₂ at temperatures > 300°C. Given the semi-quantitative nature of the SEM chemical analysis and the presence of oxygen in several compounds (gypsum, CaCO₃, SiO₂), it would have been difficult to perform a higher quality stoichiometric analysis. Regarding the particles with Sn and Cu, a good atomic proportionality (1:1) of Cu with Cl was observed, attributable to the presence of copper(I) chloride (CuCl), which might have formed due to the existence of Cl in fumes originating from the chlorine salts used in refining processes (Mora Piris 1994).

Finally, no pattern or sequence was observed regarding the intra- or inter-stratum distribution of both types of particles (rich in Sn and with Cu/Sn), which meant that the multiple analysis carried out at different depths of liming samples NF1–5 did not show any type of enrichment sequence in the content of any of these two compositional metals of bronze. Similarly, no chemical element different to those already analysed was observed, suggesting that changes in the majority raw materials used in the foundry processes and in the technological processes developed during the 16th and 17th centuries were scarce (Cockrell *et al.* 2015, 977).

CONCLUSIONS

The results obtained from the OF samples, particularly the chemical analyses carried out by μ -XRF and SEM-EDX, confirmed the assumption that, contrary to the theses advocated in traditional, insufficiently documented historical sources, there is no evidence of metal manufacturing or refining activity in the constructive elements preserved in the aforementioned area of the RAFS.

Conversely, the sequences of several liming layers overlapping with smoke deposits in the NF zone confirmed that the smelting furnaces were active over a period of time. The analyses of the NF samples were coherent with bronze smelting activity, which is well documented historically, as well as with the qualitative composition of the alloys used in the technological processes for the manufacture of military elements, mainly cannons.

No pattern was identified with respect to the intra- or inter-stratum distribution of the tin and copper/tin particles. The multiple analyses carried out at different depths of the liming in the NF samples did not reveal any type of enrichment sequence in the content of any of these two metal components of bronze. Moreover, no other chemical elements different to those already analysed were observed, suggesting little change in the majority of raw materials used in the foundry and technological processes.

Based on the historical analysis of the results, starting with the compared documentation, we can confirm that the architectural reform of the RAFS began between 1520 and 1560, with the successive projects developed by the engineers Navarro (1520), Sala (1730) and Porres (1759), of which the project by Maritz (1767) is a continuation. In 1731, a policy was initiated to acquire lands adjacent to the old installations and, at the same time, the project for a new smelting plant was undertaken, which gradually replaced—from east to west—the old metallurgical

installations dating from the 16th and 17th centuries. From Navarro's project, all graphic documentation preserved since 1725 in the Simancas General Archive contains references to a construction to the north-east that was amortized as part of the industrial complex managed by Maritz. This complex, referred to as the NF in 1925, is considered to be the OF. The explanation for the absence of patinas produced by steel manufacturing activity may lie in the documented criticism of the poor execution of the works and also because, given the unreliable nature of the construction, the furnace never came into operation or because the construction was completely renovated without manufacturing activity ever being resumed.

Finally, it is worth highlighting that the liming layers have provided an excellent fixing base for the chemical compounds emitted during the bronze smelting process, remaining stable over time, despite the partial sulfation process they have undergone. As a result, these layers underwent a transformation: from a mere coating to a historical record of the industrial activity developed during the 18th and 20th centuries in the RAFS.

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