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Understanding 17th-18th century Dutch Tin-glaze Through the Interpretation and Reconstruction of Historical Recipes

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SUMMARY:
The interest in technical art-historical sources has grown in recent years as has the awareness that they are invaluable in improving our knowledge and understanding of both the composition and degradation of art objects. This research has centred on the interpretation of Dutch 17th and 18th century tin-glaze recipes as described in contemporary, written sources. Research into the raw materials described in the recipes combined with EDX analysis of a reference group of historical tiles enabled the reconstruction of a historical glaze, the beginning of an ongoing project that is exposing new information on the nature of the fluxes used in the recipes, in particular the sodium components. The findings expand our understanding of the glazes used on Dutch tin-glaze tiles and objects.

KEY-WORDS: Tin glaze; Historic glaze recipes; Glaze reconstruction

INTRODUCTION

Researchers of historical Dutch tin-glazes are extremely fortunate in having both hand-written and published indigenous historical sources which document 17th and 18th century tin-glaze recipes as well as providing information on the production of both tin-glaze household wares and tiles. The findings presented in this paper are part of a broader PhD research into the production of Dutch tin-glaze tiles in the 17th and 18th century. While there is evidence in de archival documents that specific clay mixes and glazes were used in tile production, one has to consider tin-glaze recipes in a broader context. Although a number of production specialised in tile production, many Dutch factories produced both tiles and household wares. An initial step in the assessment and interpretation of indigenous Dutch tin-glaze recipes is to compare them with other European written sources describing tin-glaze recipes, some of which claim to document recipes from Delft.

HISTORICAL TIN-GLAZE RECIPES

The earliest records of tin-glaze recipes

Although the treatise written by Abu’l-Qasim in 1301 is considered to be the earliest text relating to tin-glaze technique, the glazes discussed are compositionally closer to alkali frit glazes. Of greater relevance is the three-part manuscript ‘The Book of the Potter’s Art’ written by the Italian Cipriano Piccolpasso (1524-1579) in circa 1558. Piccolpasso was known to have had contact with Flemish potters and there is an evident similarity between some of his recipes and techniques he documents and those found in the Dutch sources a hundred years later. Interestingly, Vannoccio Biringuccio’s published a few years earlier in 1554, describes tin-glaze recipes very similar to those found in Piccolpasso. This either suggests that Piccolpasso had taken recipes from Biringuccio’s publication, or that similar recipes were used throughout Italy at the time. A simplified overview of these recipes can be found in table I.
### Table I: Early historical tin-glaze recipes

<table>
<thead>
<tr>
<th>AUTHOR</th>
<th>DATE</th>
<th>‘MASTICOT’ (M)</th>
<th>Proportion W% in masticot</th>
<th>’TINAS’ (TA) LEAD : TIN (weight before calcination)</th>
<th>Prop. w% tinas</th>
<th>FINAL GLAZE MIX M:TA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biringuccio, Vannochio</td>
<td>1540</td>
<td>3 sand: 1 wine lees</td>
<td>10 : 3:1</td>
<td>100 : 20</td>
<td>5 : 1</td>
<td>Albertus’ 3: 1</td>
</tr>
<tr>
<td>Pilcolpasso ‘common white’</td>
<td>1558</td>
<td>30 sand: 12 wine lees</td>
<td>10 : 4</td>
<td>200 : 50</td>
<td>2 : 1</td>
<td>50: 30 + 8 salt</td>
</tr>
<tr>
<td>Diderot</td>
<td>1756</td>
<td>50 sand: 20 soda: 15 potash</td>
<td>10 : 4: 3</td>
<td>20 : 20</td>
<td>1 : 1</td>
<td>100 : 40</td>
</tr>
</tbody>
</table>

### Table II: Historical ‘Dutch’ Tin-glaze recipes

<table>
<thead>
<tr>
<th>AUTHOR</th>
<th>DATE</th>
<th>‘MASTICOT’ (M)</th>
<th>Proportion W% in masticot</th>
<th>LEAD : TIN (T) (before calcination)</th>
<th>Prop. w% tinas</th>
<th>FINAL GLAZE MIX M:T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kunckel ‘Delft’</td>
<td>1689</td>
<td>100 sand: 30 soda: 40 wine lees</td>
<td>10 : 3: 4</td>
<td>100 : 33</td>
<td>3:1</td>
<td>100: 80 + 10 salt</td>
</tr>
<tr>
<td>Sijbeda (average of recipes)</td>
<td>1721</td>
<td>300 sand: 60 soda: 36 potash</td>
<td>10 : 2: 3</td>
<td>200 : 60</td>
<td>3:1</td>
<td>100 : 66 + 22 salt</td>
</tr>
<tr>
<td>Diderot ‘Blanc de Hollande’</td>
<td>1756</td>
<td>50 sand: 20 soda: 15 potash (+ 6 oz. manganese)</td>
<td>10 : 4: 3</td>
<td>20 : 20</td>
<td>1:1</td>
<td>100 : 40</td>
</tr>
<tr>
<td>Frese Albertus (Translation of Kunckel)</td>
<td>1774</td>
<td>100 and 30 soda: 40 potash</td>
<td>10 : 2: 4</td>
<td>100 : 33</td>
<td>3:1</td>
<td>100 : 80 + 10 salt (+ cobalt and copper filings)</td>
</tr>
<tr>
<td>Paape</td>
<td>1794</td>
<td>500 sand: 30 soda: 60 salt</td>
<td>10 : 0,6: 1,2</td>
<td>10 : 3</td>
<td>3:1</td>
<td>65 : 50 (+ 0,5 smalt and copper filings)</td>
</tr>
</tbody>
</table>

### Recipes specifically relating to Dutch tin-glaze production

The significance of the indigenous Dutch sources that document historical Dutch tin-glaze recipes have been discussed in previous publications. The most quoted text relating to Dutch tin-glaze production is Gerrit Paape’s treatise ‘De Plateelbakker of Delftsch’ published in 1794. Paape (1752 – 1803) worked as an apprentice decorator in a Delft faience factory from the age of 13 for a number of years, after which he worked as a journalist and writer. In this treatise he describes the materials and techniques used in the Delft faience industry at that time. However, arguably the most significant historical source regarding Dutch tin-glaze recipes is a 160-page parchment-bound, hand-written notebook kept in the archive of the Museum Hannemahuis in Harlingen (see figure 1). The notebook was written between 1712 and 1720 by Petrus Sijbeda (ca.1670 - ca.1721) a factory-owner from a family of Harlingen potters. In the notebook Sijbeda documents over 80 recipes from his father and other factories for tin glaze, coperta (lead) glaze (kwaart), on-glaze colours and kiln glaze (binnenverf), as well as providing recipes for clay mixes suitable for tiles (stenen), tableware (schuttels) and kiln bricks (boogstenen). The glaze recipes he describes are primarily from Harlingen, but some are also attributed to other production centres, notably Delft, Utrecht, Rotterdam, Makkum and even England. In certain cases the specific potters’ names that are linked to glaze recipes have been shown to be historically accurate. Many recipes are also dated, ranging from 1659 to 1720. Sijbeda describes the quality of the different glazes and clay mixtures and often the source and cost of materials. Another similar written source that is only available in transcript is the hand-written oven-book of another Harlingen potter Sijbrand Feitema, dated 1725.
Historical Dutch tin-glaze recipes can also be found in other European written sources (see Table 2). The recipes are generally attributed to Delft which was the most important centre of faience production at the time. The German scientist, alchemist and glass maker, Johann Kunckel, (1637?-1703), published a treatise in 1679 in which he provides 60 recipes for glass and glaze, allegedly collected in the Netherlands. The treatise was translated into Dutch in 1774 by an author under the name of AF, possibly the painter Albertus Frese (1714 – 1788). Information from Kunckel’s treatise was used for Diderot and d’Alembert’s entry on ‘Fayence’ in the well-known ‘Encyclopédie’ published in 1756.\(^8\)

**Dutch Tin-glaze recipes in historical context**

Looking at the historic recipes one is struck by the similarities in terminology and composition, despite the fact that the recipes cover 250 years and are from authors from different countries that have quite different backgrounds and experience. Almost all the sources describe the tin glaze as being made from two compounds which were made separately: a glass frit (masticot in Dutch, marzocatta in Italian) and calcined lead and tin (tin ash or tinas in Dutch but only vaguely referred to as tin or latta in Italian). Masticot was a mixture of sand (quartz) and flux (soda and/or potash and common salt), which was melted on the bottom of the main kiln before being broken up and ground into a powder to make a frit. The second lead-tin mixture (tinas) was produced from lead and tin metal blocks which were weighed to specific proportions before being calcined in a separate tinas oven or tin oven (necessary due to the emission of sulphur that would affect the glaze firing). The masticot and tinas powders were then combined, usually with added salt and/or potash, before again being melted on the bottom of the kiln (in a crucible in Italy and piled within a ‘wall’ of masticot powder in the Netherlands). The melted mass was then milled, mixed with water, and applied to the fired ceramic.

The glaze recipes were all measured in weight, generally in pounds (lb). The weights are proportional as weight measurements, (measurements in ‘pounds’ would have varied between countries and even cities). The masticot mixes appear to fall into two main groups. In the Italian recipes, the proportion of sand to flux in the masticot is around 10 : 4. This is similar in Sijbeda’s recipes. However, while Paape’s masticot recipe contains far less flux, the proportion of flux in Kunckel’s ‘Delft’ recipe is double that of the first group. This is reflected in Diderot’s and Albertus’ ‘Dutch’ recipes, which is not surprising considering that they sourced their information from Kunckel. Kunckel’s ‘Delft’ recipe is made even more questionable as it describes the use of wine lees (also known as tartar), the source of potash used in the wine-producing regions of the south. Also, the proportions of tinas to masticot in Kunckel’s final glaze recipe is exceptionally high.

The proportional weight of lead and tin used to produce the tinas in the Dutch recipes is less variable, consistently giving proportions of 3:1 of lead and tin. The one exception is found in Diderot who documents the use of equal proportions, also seen in some of the earlier Italian recipes, which may suggest a lower tin purity. While it appears possible to divide the documented historical tin-glaze recipes into groups, one must be aware that these are simplified recipes. Piccolpasso describes a number of recipes from different Italian regions, which vary considerably, assumedly due to variations in the raw materials from the different geological areas.
INTERPRETING 17TH & 18TH CENTURY DUTCH TIN-GLAZE RECIPES

Having demonstrated that the Sijbeda tin-glaze recipes make sense within an historical framework, the next step was to attempt to interpret the meaning of the terms used in the recipes in order to understand the composition of the materials they describe. To do this one has to consider the sources and availability of raw materials at the time as well as the methods of extracting and refining these raw materials, taking into account probable variations in quality.

Sand
Sand provides an easily available source of silica (SiO₂) for the production of glass and glaze. Sand is ground stone with a grain size varying from 0,125mm for very fine sand (125µm) up to 1mm for coarse sand. In general sand consists primarily of silica due to silica’s chemical inertness, hardness, and resistance which results in a slower process of weathering. Sand often contains other common elements such as iron (Fe₂O₃), calcium carbonate (CaCO₃) and feldspar (aluminosilicates rich in K, Na or Ca). Such impurities may not only affect the colour of the final glaze, but also function as fluxes at higher temperatures, (especially feldspar and calcium). In the historical recipes we see that Diderot recommends the use of sand from Nevers which is known to have a high CaCO₃ w%. Sijbrand Feijtema mentions that sea sand was used in the Harlingen factories, commenting that sand from Terschelling (an island in Friesland) produces a poorer product than sand from The Hague (also known to have a high CaCO₃ content).

Soda
The Dutch recipes all contain soda or zouda. The term soda suggests that the material being added was sodium carbonate, a common product that was easily available. Soda had been produced and traded for centuries to make soap, to bleach textiles and to make glass.

Barilla
The earliest European glassmakers of Venice sourced soda from salt-tolerant (halophyte) desert or sea plants of the genus Salicornia, such as Salsola soda, known as barilla, from the salty morasses of the Mediterranean Sea. The best quality barilla comes historically from Alicante in Spain. Alicante zouda is specifically mentioned in a number of the early glaze recipes in Sibeda’s notebook. Salsola soda contains a relatively high sodium carbonate content (30 – 40%) together with some potassium, calcium and magnesium carbonates.

Kelp
In the early period of tin-glaze production in the 16th to mid 17th century the main source of soda to make glaze would have been imported barilla. From the mid-17th century, local sources of sodium carbonate became available in Northern Europe extracted from seaweed, primarily from cold-water seaweed from the Laminariaceae family, known as kelp, and the Fucus family, known as wrack. Sijbeda specifies the use of engelse soda (English soda). One can assume that this refers to soda produced from kelp. These recipes date from about 1670 which is the period that the kelp industry in Britain was rapidly developing. Kelp was first harvested and calcined by burning in the Scilly Islands but during the 1700’s Scotland became the main supplier.

In 1750 Sijbrand Feytama described glaze recipes containing both Alicantsche zouda and Schotsche soda (Scottish soda). In the same period Diderot provides a recipe for English white (tin-glaze) using soda made from Normandy seaweed. The amount of sodium carbonate that can be extracted from kelp or wrack is far lower than from Barilla. Robert Brill analysed a number of North Sea wrack samples concluding that they produced equal amounts of Na and K (oxides), which constituted between 29.2-40.7% of the total ash. Similarly, there were equal amounts of Ca and Mg (10.7-22.8% of the total ash). He referred to the glasses produced with kelp as a flux as being ‘mixed-alkali’.

In the Sijbeda recipes containing Alicante soda, not only is the w% of soda generally lower, but potassium in the form of pot-as (potassium ash) or wied-as (plant ash) is always added, resulting in a similar mixed-alkali glaze frit. In 1823 Feytama commented that one only has to use half the Alicante soda as it is not as ‘fat’ as the Scottish soda. Brill mentions the fact that there would have been variations in the composition of kelp or wrack depending on where and how it was harvested and at what time of year. The fact that it was a question of trial and error can be seen in a Sijbeda recipes dated 1718 where different percentages of English soda are recommended depending on whether the soda is ‘strong’ or ‘weak’. Similarly, year later in 1719 a higher percentage of soda in a recipe is explained by the fact that the soda is ‘weak’. Sijbeda states that if the soda used was of poor quality, the glaze would be ‘dry’, presumably meaning that it would lack shine.

4
Potash
Potash (K) is used in glass and glazes in the carbonate form (K₂CO₃), known as pearl ash or in the form of tartar. Wine lees, or ‘cream of tartar’ is a by-product of winemaking and a common source of potassium in winemaking regions, primarily consisting of Potassium bitartrate (K₂C₄H₄O₆). Piccolpasso discusses three types of deposits that accumulate in wine barrels: tartar, argol, and lees. Ashes of wine lees can contain as much as 90% potassium carbonate. Potash is also obtained in the form of potassium carbonate or potassium hydroxide from wood ash (generally beach, pine or birch) and other plants such as ferns and heather. The wied-as or pot-as mentioned in Dutch sources suggests that potash was sourced from wood ash or ferns.

Lead
Lead oxide (PbO) has been used to create glazes for thousands of years. It is easy to apply and forms a glass at a low temperature. To produce the tinas, lead and tin metal blocks were heated in a separate (tinas) oven with tin. When pure lead is heated a yellow, amorphous powder forms on the surface known as litharge (lead(II)oxide). This was scraped off as it formed in the kiln. The Dutch terms for litharge were loodglit, goudgelit or loodas. Sijbeda shows that that lead metal was obtained from different sources and was of different qualities. As well as lood (lead), he mentions the use of theelood (tea lead from tea chests) and oude plat lood (old lead sheet). In the pure lead-glaze or kwaart recipes, the use of goudgelit (litharge) was always specified.

Tin
As with lead, potters calcined tin metal in an oven to make tin oxide (SnO₂). The sources of tin were limited in the 17th and 18th century. The high quality of the tin from Cornwall in England had been known since the Romans and is mentioned by both Piccolpasso and Sijbeda. Sijbeda describes variations in the quality of tin used for the glazes using the terms fijne tin (good quality tin) and keur tin (standard quality tin). He states that after English tin, the next best quality was from the province of Holland (two provinces in the west of the Netherlands) and the poorest from local suppliers in Friesland (the province in which Harlingen is situated). The different quality of glazes recorded by Sijbeda, ranging from sleghit (poor) to high quality wit wit, (white, white) appears largely related to the proportion of tin. Sijbeda noted that the best quality tin glaze has such a high proportion of tin that it is too expensive to be practical, although he later comments that it is worth using a good quality glaze as the wares can then be sold for a higher price. Tin was probably the most expensive ingredient in tin-glaze and potters did their best to use as little as possible.

Figure 2 shows the w% of tin used in the dated glaze recipes in Sijbeda. The quantities refer to the tin before calcination as a percentage of the final glaze mix. The final amount of litharge produced would have been dependent on the purity of the tin used. Taking into account the weight change during calcination, the tin w% is seen to range between 7 and 11. In the two recipes where a lower tin w% is documented, one (A) is said to be of poor quality and the other (B) used for an unmixed clay with a lower CaCO₃ content. In the one example where a high percentage of tin is used (C), impure tin solder was used. Interestingly, while the w% of tin metal appears to remain fairly consistent in the recipes, proportion of tinas used in the final glaze mix (as seen in the recipes) appears to increase slightly over time, possibly suggesting that the quality of the tin used may have decreased.

Salt
When the ground masticot and tinas powder were combined to make the glaze, common salt or zout was generally added in a ratio of approximately 10:6 by weight before being melted in the kiln. The proportion of salt used in the final glaze mix in Sijbeda’s recipes remained consistently around 8 w% in the later recipes. Salt
is found in almost all historical tin-glaze recipes including those in Pilcolpasso, Diderot and Kunckel. We know that the ‘salt’ referred to is sodium chloride due to the fact that it is often referred to as ‘sea salt’. Of the 76 glaze recipes in Sijbeda only three recipes do not include salt in the final mix. These, including the oldest dated recipe dated 1659, are all referred to as being poor quality glazes. Only two recipes in Sijbeda dated 1812 and 1815 include salt in the masticot, as does the recipe in Paape.

There does not seem to be a logical explanation as to why salt was added when the soda used, since both are a source of sodium. One consideration was that the salt was cheaper, but the references to the advantages of using imported Portuguese salt from St Ubes show that cost was not the main issue. Bastenaire-Daudenart\(^1\) states that while one can replace the soda with sea salt, the sand will not fuse as well with salt as with Alicante soda. The different chemical formulations of salt and soda result in different reactions in the kiln. NaCl melts at 801°C at which point chlorine gas is emitted, a reaction that occurs fairly quickly. Sodium carbonate (Na\(_2\)CO\(_3\)) melts at 851°C and undergoes thermal decomposition resulting in the formation of NaO and CO\(_2\). This process is slower, possibly providing more time for the sodium to react with the silica.

Salt is clearly considered to be of an advantage in the glaze mix. At one point Sijbeda claims that the proportion of salt is responsible for the whiteness of the glaze. This idea was supported by Bastinaire – Daudenart when he claimed that (common) salt was more important than soda or potash for the production of tin glaze. Franchet was still supporting this idea in 1911.\(^*\) Bastinaire claims that, although soda works better as a flux, salt has the advantageous property of bleaching the glaze. He suggests that the reaction on heating and consequent emission of hydrochloric acid results in fusion of the tin, lead and silica, as well as the elimination of unwanted substances in the glaze, thereby ‘retaining the beauty of the product.’ He appears to suggest that a reaction occurs that dissolves unwanted discolouring material in the glaze. This idea is supported by Prudence Rice,\(^19\) who states that sodium chloride in ta glaze mix results in the vaporisation of traces of iron oxide with chlorine emissions during firing. The quality of the salt is also shown to have been an issue. In 1770 Tjallingui complains that plates and tiles were discoloured *vol blauw* (completely blue) due to the use of *allemattes zout* (common salt) rather than imported sea salt from St Ubes in Portugal.

**Colourants**
Both Albertus and Paape mention the addition of small amounts of cobalt oxide in the form of smalt and copper filings in the Delft glazes. It is presumed that this was done either to whiten a yellow-tinted glaze, or to attempt to achieve a colour closer to that of Chinese porcelain glazes.

**COMPARISON OF THE RECIPES WITH THE PHYSICOCHEMICAL ANALYSIS OF DUTCH TIN-GLAZE TILES**

Another means of assessing the glaze recipes in the source documents is by comparing the composition described in the recipe with data on the elemental composition of Dutch historic tin-glaze tiles from the period under study. A set of historical tiles was selected with a range of manufacture dates and production centres (see figure 3). The provenance of Dutch tiles is notoriously problematic, and the primary criteria was to find tiles where the centre of production could be determined with as much certainty as possible. The determination of provenance was made based on the decorative style, documentation, the history of the building where tiles had been removed, or excavation data. The tiles were acquired on loan from museums or private collectors. Kiln waste from Harlingen and Rotterdam was also sourced. Three specific production centres were chosen: Rotterdam, Harlingen and Utrecht. Apart from being important production centres, Rotterdam and Harlingen were chosen due to the fact that the majority of historical archival sources are linked to these cities. Delft tiles were not chosen as Delft was not a major producer of tiles, quickly specialising in faience objects. In addition, provenance of early Delft tiles is notoriously problematic.

![Figure 3: Overview of tile selection analyzed with SEM-EDX](image)

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\(^1\)Bastenaire-Daudenart 1911.
\(^*\)Bastinaire claims that although soda works better as a flux, salt has the advantageous property of bleaching the glaze.
\(^19\)Prudence Rice.
SEM-EDX analysis

Scanning electron microscopy (JEOL 9510LV E) coupled with an energy-dispersive X-ray detection system (Thermo Noran system 6) was used to obtain microstructural and elemental characterization of the tile set. Analysis was performed at low vacuum (30 Pa), 10-20 kV high voltage and a working distance of 10 mm. All cross-section samples were imaged in back-scatter mode which provided information on the morphology of the glazes. Semi-quantitative data on the elemental composition of the glazes was obtained with energy-dispersive X-ray detection. Concentrations are reported as oxides of elements as ceramics and glass materials primarily contain elements in the form of oxides.

Sampling

Three samples of about 1 mm (the samples included both the glaze and ceramic body) were taken from different areas of each tile using a drill with a 1 cm diamond disk. The samples were embedded in Epofix epoxy resin and polished using silicon carbide paper to 4000 mesh. EDX measurements were taken of three areas of the glaze and the average calculated.

Results

The back-scattered SEM images (see figure 4) show examples of how the homogeneity of both the glaze and ceramic tile improved during the 17th and 18th century. The EDX data of the glaze composition was normalised to take into account the influence of the epoxy embedding material on the C and O measurements. Figure 5 gives an overview of the w% of the composition of the historic tile glazes dated between 1600 - 1750 as oxides (SiO₂, PbO, SnO₂, Na₂O, K₂O, and CaO). Although the elemental composition is seen to vary, certain patterns can be observed. The w% of silica remains fairly constant at +/- 50%, K₂O at 3 - 5%, Na₂O at 2 - 3% and CaO at 4%. The SnO₂ w% is variable, ranging from 6 – 12 w%. There appears to be a slight increase in the w% of tin over the period which could be seen to reflect the increase seen in the Sijbeda recipes in figure 2.

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Figure 4: SEM backscattered images showing the change in glaze and ceramic morphology of Dutch tiles in the period; Rotterdam +/- 1620 (above), Utrecht +/- 1720 (below)

Figure 5: Comparative overview of the w% of major elements (reported as oxides) in the reference group of Historical Dutch tin-glaze tiles 1600 – 1720 (SEM-EDX, JEOL 9510LV E, low vacuum 30pa)
RE-INTERPRETATION AND RECONSTRUCTION OF A RECIPE – A PILOT STUDY

The information gained from research into the raw materials and the chemical analysis of the historic tile glazes was used to re-interpret one of the Sijbeda glazes in order to make a glaze reconstruction. The aim of the reconstruction was to assess in how far the new information regarding the raw material composition could be supported.

‘A good glaze from my father’

The re-interpretation of a recipe

The glaze recipe chosen for reconstruction was a Harlingen recipe from page 9 in Petrus Sijbeda’s glaze book (see figure 6). Sijbeda writes that the recipe was used by his father to make tiles ‘bij mijn vader tot de fijn steentjes gebruikt’ (used by my father to make good quality tiles). The recipe was calculated taking into account the interpretation of the ‘soda’ as a mixed-flux. In addition, 6.0 w% CaCO₃ was added to compensate for the 4% CaO found in all the historical glazes which would have been present in the kelp ash and possibly also the sand. When using the EDX results to calculate a glaze recipe, the calcium, sodium and potassium oxides had to be recalculated to represent carbonates. Similarly, the slight difference in w% between the lead and tin proportions that would have occurred once they were calcined had to be taken into account. The composition of the glaze that would result from the re-interpreted recipe was compared with the average chemical composition of historic glazes (see table III). As can be seen, the interpretation of the ‘soda’ as a mixed-flux brings the composition closer to that of the historic glazes, although the sodium w% was still somewhat higher in the recipes than in the historical glazes. The main reason for this is considered be the impurity of the soda as the kelp would not have consisted of pure carbonates.

The glaze reconstruction

The glaze reconstruction protocol followed the historical processes as closely as possible within the feasible health and practical limitations. The glaze was produced in two stages as described. The process of calcining tin and lead in an open oven was not attempted due to health and safety issues. Silver sand that contained less than 1 w% iron and calcium was used as the zand in the recipe. Pure sodium and potassium carbonates were used for the soda as a mixed flux and calcium carbonate was used for the calcium. The finas was made up from pure litharge (PbO) and tin oxide. Sea salt was used for the zout in the recipe. When calculating the ingredients, the lead and tin quantities had to be recalculated as the recipes refer to the metal state whereas the oxides created by calcining were used for making the final glaze mix. Table 3 shows how the glaze recipe was calculated and compared the expected fired glaze composition with the EDX analysis results of historical Dutch tiles glazes.

Figure 6: Recipe on page 9 of Sijbeda’s recipe book described as a glaze ‘used by my father for good quality tiles’.
Making the masticot and final glaze

The melting of the masticot and glaze mixes was undertaken in a well-ventilated gas kiln. The components of the masticot recipes were mixed and piled-up on a bed of sand on the bottom of a gas kiln (see figure 7). The firing protocol was formulated from what is known about the kilns and firing procedures of the period. The kiln was heated at 100˚C per hour up to 700˚C. The kiln was then brought up to 1000˚C where the temperature was held for 30 minutes before leaving the kiln to cool naturally. The masticot was ground in a granite mortar and passed through a 800 µm mesh. It was then mixed with the tinas mixture and the firing process was repeated. The glaze powder was mixed with demineralized water and applied in a thickness of 0.8 mm to ceramic test tiles that had already been produced from historical clay recipes with CaCO₃ weight percentages of 20, 30 and 40%.

Table III: Calculation of the ‘good’ Sijbeda recipe together with a comparison of the estimated final glaze composition with the average results of EDX analysis of historical glazes. (These calculations are based on the raw materials being pure).

<table>
<thead>
<tr>
<th>Composition and source</th>
<th>Recipe in Text (in lb) (fluxes as carbonates)</th>
<th>Calculation of glaze adjusted to known raw materials (fluxes in recipe calculated to oxides)</th>
<th>Recipe + 6 to match the quartz w% in the EDX results (oxides)</th>
<th>Average w% from EDX of historic tiles (oxides)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘sand’ Impure quartz</td>
<td>300</td>
<td>300</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>‘soda’ Kelp +/- 50:50 Na₂CO₃/K₃CO₃</td>
<td>200 carbones in recipe = 126/lb oxides</td>
<td>63 Na₂O</td>
<td>10,5 (includes 4% from salt = 6,5)</td>
<td>2,5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>63 K₂O</td>
<td>10,5 (-4% CaO7 = 6,5)</td>
<td>4</td>
</tr>
<tr>
<td>CaCO₃ calcium in sand or plants</td>
<td>Not in recipe</td>
<td>(4% CaO= 6,8 CaCO₃)</td>
<td>+4</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TINAS Glaze mix = 3:2 masticot: tinas (66%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘ood’ Lead (metal) 200 (Calcination x 1,08)</td>
</tr>
<tr>
<td>‘in’ Tin (metal) 100 (Calcination x 1,27)</td>
</tr>
</tbody>
</table>

| ‘out’ NaCl 65 (11,5%) | 65 NaCl = 34,9% Na₂O | 4 % Na₂O | - |

Figure 7: Masticot (left) and glaze mix (right) before and after firing
Comparing the glaze tests with historical tiles

Figures 8 and 9 show the results which are now undergoing investigation. As can be seen, a successful glaze was achieved. The CaCO$_3$ w% of the ceramic body appears to work as a flux and have an influence on the gloss of the final glaze. Further tests are being undertaken to assess the influence of variation in firing temperature.

When comparing the EDX results with those of an historical Harlingen glaze from the same period the similarity is evident although the w% of sodium is still too high with relation to that of potassium. In addition, the magnesium is missing in the composition of the glaze test. The silver sand used clearly did not contain any significant amounts of magnesium which, as the potassium most probably came from the kelp. In addition, the glaze reconstruction has relatively large tin oxide crystals and the interface is broader – probably due to the high w% of sodium in the glaze which is a particularly effective flux.

**CONCLUSIONS**

The research into raw materials, recipe re-interpretation, glaze reconstruction and preliminary glaze tests have provided significant new insight into the composition, sources, and influences of the raw materials used in Dutch tin-glaze production. Of particular interest is the source of the ‘soda’ in historic recipes which from the later 17$^{th}$ century was extracted from kelp and wrack and would in fact have been a mixture of sodium and potassium carbonate. Also of interest is the significance of the sodium chloride added to the final glaze mix. Both issues are the subject of continuing research. When interpreting historic glazes, it is clearly essential to consider the composition with the purity of the materials described. The high w% of sodium in the glaze is certainly due to the fact the kelp ash would not have consisted of pure oxides but would have contained unburnt and carbonaceous matter. The variation in the composition of the kelp and wrack over the year is now under investigation. It is probable that sodium/potassium ratio varied which may explain the low w% of the K in the reconstructed glaze.
REFERENCES

4 VAN LOOKEREN CAMPAGNE, Een verkeerde loop in ‘t vuur: an initial investigation into what Dutch archival sources can tell us about techniques and problems in the production of 17th and 18th century Dutch tin-glaze tiles. GlazeArch2015, LNEC, Lisbon
7 FEIJTEMA, S. Aenmerkingingen Rakende de Gleijbakkerij [1725]. Transcript, Museum Hannemahuis.
8 KUNCKEL, J. ‘Von dem Hollandischen, oder (so genannten) Barcellanischen, Weissen und bunten Topffer-Glasur-un Mahlerwerk’ in Ars Vitaria Experimentalis, Oder Volkommene Glasmacher-Kunst, Frankfurt/Leipzig, 1679
9 FREESE, A. Proefkundige Verhandeling van Wit En Gecouleurd Platiel Verglas En Schilderwerk; Benevens Eene Duidelyke Onderrichting van Het Glas-Schilderen, ’s-Gravenhage: H. H. van Drecht, 1774
11 Sijbeda 1712 p 3,7,9,122
14 Diderot p 1751 p456
16 Sijbeda 1712 p153 - 155
17 BASTINAIRE – DAUDENART, F. L’Art de fabriquer la faïence recouverte d’un émail opaque blanc et coloré, La Librairie Scientifique et Industrielle, De Malher et C°, Paris, 1828
18 FRANCHET, La Fabrication Industrielle des Emaux et Couleurs céramique, Paris 1911, p 84
19 RICE, P. - Pottery Analysis : A Sourcebook. Chicago etc.: Chicago etc., =University of Chicago
21 VAN LOOKEREN CAMPAGNE, K. – ‘Not too white’: an investigation into the influence of the use of calcium carbonate-rich imported marls on 17 - 18th century Dutch tin-glaze tile production TECHNART2018 (Non-destructive and Microanalytical Techniques in Art and Cultural Heritage), Bilbao, Spain. Book of Abstracts