

## **ADDITIONAL FILE FOR:**

### **The white of the 20<sup>th</sup> century – An explorative survey into Dutch modern art collections.**

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# Introduction

Table S1 indicates the titanium white pigments used in the 1920s and the 1940s. This information is referred to in the paper introduction.

**Table S1: Pigment compositions of the 1920s and 1940s reproduced from Laver [1]**

| Pigment compositions of the 1920s |                                                                                   |                                           | Pigment compositions of the 1940s |                                                                                                       |                              |
|-----------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------|-----------------------------------|-------------------------------------------------------------------------------------------------------|------------------------------|
| Product name                      | Composition                                                                       | Comments                                  | Product name                      | Composition                                                                                           | Comments                     |
| Kronos Prima X                    | 83% TiO <sub>2</sub>                                                              | Fredrikstad 1918/1919                     | Titanox A                         | Anatase + small amounts of alkaline phosphate                                                         | Untreated except for milling |
| Kronos Extra X                    | 65%/69% TiO <sub>2</sub> -25% CaPO <sub>4</sub> -10%BaSO <sub>4</sub> (composite) | Fredrikstad, replaced Prima grade in 1919 | Titanox A 168                     | Anatase 1% Al <sub>2</sub> O <sub>3</sub> coating                                                     | No organics                  |
| Kronos Standard X                 | 25%-30% TiO <sub>2</sub> /5% CaPO <sub>4</sub> /70% BaSO <sub>4</sub> (composite) | Fredrikstad                               | Titanox AA                        | Anatase Calcinated with 1% Sb <sub>2</sub> O <sub>3</sub> , 1% Al <sub>2</sub> O <sub>3</sub> coating | No organics                  |
| Kronos Standard A                 | 25%-30% ZnO + 70% Standard X                                                      | Blended in Europe                         | Titanox C                         | 30% anatase/70% CaSO <sub>4</sub> (composite)                                                         |                              |
| Kronos Extra A                    | 30% ZnO + 70% Extra X                                                             | Blended in Europe                         | Titanox B                         | 25% anatase / 75 % BaSO <sub>4</sub> (composite)                                                      |                              |
| Kronos Standard T                 | 25% TiO <sub>2</sub> /75% BaSO <sub>4</sub> (composite)                           |                                           | Titanox B-30                      | 30% anatase / 70 % BaSO <sub>4</sub> (composite)                                                      |                              |
| Kronos Extra T                    | 50% TiO <sub>2</sub> /50% BaSO <sub>4</sub> (composite)                           |                                           | Titanox A-NC                      | Rutile recalcinated with 1% ZnO coated with 1%-2% Al <sub>2</sub> O <sub>3</sub> and                  | 1939                         |
| Blanc de Thann or EB              | 98%-99% pure                                                                      | Thann (from 1923)                         | Titanox RC-HT                     | 30% rutile/CaSO <sub>4</sub> composite                                                                | Introduces in late 1940      |
| Blanc de Thann or P               | 98% TiO <sub>2</sub>                                                              | Thann (from 1923)                         | Titanox RC                        | 30% rutile/70% CaSO <sub>4</sub>                                                                      | 1941                         |
| Blanc de Thann                    | Mixtures with BaSO <sub>4</sub> and ZnO                                           | To meet market requirements               | Titanox M                         | 30% TiO <sub>2</sub> with Magnesium silicate                                                          |                              |
| Titanox A                         | 98% TiO <sub>2</sub>                                                              | Niagara Falls after 1926                  | Titanated lithopones              | 15% TiO <sub>2</sub> , 25% ZnS, 60% BaSO <sub>4</sub>                                                 |                              |
| Titanox BX                        | 16% TiO <sub>2</sub> /84% BaSO <sub>4</sub> (composite)                           | Niagara Falls                             |                                   |                                                                                                       |                              |
| Titanox BXX                       | 25% TiO <sub>2</sub> /75% BaSO <sub>4</sub> (composite)                           | Niagara Falls                             |                                   |                                                                                                       |                              |
| Titanox C                         | 28-35% TiO <sub>2</sub> / 72-65% CaSO <sub>4</sub> (composite)                    | Niagara Falls                             |                                   |                                                                                                       |                              |
| Other products                    | Titanated lithopones barytes and gypsem (ca. 15% TiO <sub>2</sub> )               | From 1926                                 |                                   |                                                                                                       |                              |

# Experimental – Paintings dataset

Prior to processing, the data were organized into well-structured tables. Each painting ('art') and reference ('ref') received a unique three digit number (such as 'art\_005' or 'ref\_011'). Hence each object has the following structure: objecttype\_3digitnumber. As multiple XRF spectra were taken from one object as well as supporting analysis each separate analysis named a 'sample' and is structured: objecttype\_3digitnumber-analysisistype\_3digitsnumber such as 'art\_001-xrf\_005' indicating the fifth XRF spectrum of the first artwork. For the additional analysis carried out multiple times but on one micro sample all data are interpreted as one analysis and these samples are thus labelled for example 'art\_006-xrd'. All samples containing 'xrf' have a related csv file named identically and can be processed by PyMCA.

The paintings dataset used in this study is shown in Table S2.

**Table S2: Paintings dataset**

| Artwork ID | Artist          | Title                         | Year | Collection | Binding medium | Instrument | # spectra | Sample yes/no |
|------------|-----------------|-------------------------------|------|------------|----------------|------------|-----------|---------------|
| art_001    | hunziker        | compositie                    | 1965 | rce        | oil            | 1          | 2         | N             |
| art_002    | freijmuth       | het vierkant                  | 1976 | rce        | acrylic        | 1          | 7         | N             |
| art_003    | ruijter         | no 36                         | 1975 | rce        | acrylic        | 1          | 3         | N             |
| art_004    | gerrits         | compositie 6.56               | 1956 | rce        | oil            | 1          | 8         | N             |
| art_005    | markus          | portret dr. ir. j.m.m. ritzen | 1992 | rce        | oil            | 1          | 3         | N             |
| art_006    | de vries        | marjola                       | 1942 | rce        | oil            | 1          | 4         | N             |
| art_007    | wittenberg      | amaryllis                     | 1931 | rce        | oil            | 1          | 4         | N             |
| art_008    | lucebert        | kadettenfeest                 | 1977 | rce        | acrylic        | 1          | 3         | N             |
| art_009    | van der heijden | najaarslandschap              | 1958 | rce        | tempera        | 1          | 3         | N             |
| art_010    | van der heijden | avond                         | 1959 | rce        | oil            | 1          | 4         | N             |
| art_011    | van der heijden | tweeluik                      | 1964 | rce        | oil            | 1          | 3         | N             |
| art_012    | van der heijden | kruis                         | 1965 | rce        | unreported     | 1          | 5         | N             |
| art_013    | henkes          | portret van albert breur      | 1964 | rce        | oil            | 1          | 4         | N             |
| art_014    | henkes          | stilleven                     | 1956 | rce        | oil            | 1          | 3         | N             |
| art_015    | henkes          | stilleven van bloemen in vaas | 1952 | rce        | oil            | 1          | 2         | N             |
| art_016    | henkes          | mesdinaar                     | 1940 | rce        | oil            | 1          | 5         | N             |

|         |                 |                                |         |     |             |   |    |   |
|---------|-----------------|--------------------------------|---------|-----|-------------|---|----|---|
| art_017 | henkes          | winter in groningen            | 1972    | rce | oil         | 1 | 3  | N |
| art_018 | schotel         | haven douarnenez               | 1930    | rce | oil         | 1 | 3  | N |
| art_019 | appel           | binnenhaven in de sneeuw       | 1940    | rce | oil         | 1 | 4  | N |
| art_020 | appel           | ophaalbrug amsterdam           | 1942    | rce | oil         | 1 | 2  | N |
| art_021 | corneille       | compositie I                   | 1958    | rce | oil         | 1 | 3  | N |
| art_022 | van der heijden | hellende horizon               | 1978    | rce | acrylic     | 1 | 4  | N |
| art_023 | van der heijden | blauw kader                    | 1980    | rce | acrylic     | 1 | 4  | N |
| art_024 | van der heijden | compositie zwart wit nr 24     | unknown | rce | oil         | 1 | 3  | N |
| art_025 | van bohemien    | the game                       | 1967    | rce | oil         | 1 | 3  | N |
| art_026 | van bohemien    | witte compositie               | 1956    | rce | oil         | 1 | 4  | N |
| art_027 | willink         | groene dame                    | 1930    | rce | oil         | 1 | 3  | N |
| art_028 | wouters         | zelfportret in witte kiel      | 1938    | rce | oil         | 1 | 3  | N |
| art_029 | kvapil          | les environs de bruxelles      | 1930    | rce | oil         | 1 | 5  | N |
| art_030 | rajlich         | structurr in groen             | 1972    | rce | oil         | 1 | 3  | N |
| art_031 | nieuwenhuijs    | witte poedel                   | unknown | rce | oil         | 1 | 3  | N |
| art_032 | hussum          | mask                           | 1944    | rce | oil         | 1 | 1  | N |
| art_033 | wolvencamp      | compositie orion               | unknown | rce | oil         | 1 | 3  | N |
| art_034 | appel           | dorp in de winter              | 1942    | rce | oil         | 1 | 3  | N |
| art_035 | akkerman        | landschap                      | 1969    | bfk | oil         | 1 | 5  | Y |
| art_036 | vunderink       | untitled                       | 1985    | bfk | acrylic     | 1 | 5  | Y |
| art_037 | baumgartner     | untitled                       | 1986    | bfk | oil         | 1 | 4  | N |
| art_038 | van arkel       | hollands diep 4                | 1991    | bfk | oil         | 1 | 4  | N |
| art_039 | breevoort       | untitled                       | 1995    | bfk | oil         | 1 | 7  | N |
| art_040 | byron           | japanese industrialist 3       | 1989    | bfk | oil         | 1 | 7  | N |
| art_041 | van der heijden | hellende horizon               | unknown | bfk | acrylic     | 1 | 3  | Y |
| art_042 | hillenius       | voorjaar                       | 1991    | bfk | oil         | 1 | 7  | N |
| art_043 | lataster        | untitled                       | 1987    | bfk | spray paint | 1 | 3  | N |
| art_044 | lucassen        | inside outside                 | 1995    | bfk | oil         | 1 | 8  | N |
| art_045 | lucassen        | no                             | unknown | bfk | unreported  | 1 | 3  | N |
| art_046 | lucebert        | alle schatten komen uit afrika | 1985    | bfk | oil         | 1 | 9  | Y |
| art_047 | van bohemien    | vrouw ruikt bloemen            | 1975    | bfk | oil         | 1 | 10 | Y |
| art_048 | roeland         | planten VII                    | 1986    | bfk | oil         | 1 | 4  | N |
| art_049 | van golden      | tweeluik                       | 1965    | bfk | spray paint | 1 | 1  | Y |
| art_050 | tutzina         | untitled                       | 2000    | bfk | unreported  | 1 | 1  | Y |
| art_051 | hunziker        | compositie blauw groen         | 1955    | amc | unreported  | 1 | 7  | N |
| art_052 | appel           | compositie van kleur pallet    | 1965    | amc | unreported  | 1 | 10 | N |
| art_053 | wagemaker       | stilleven in rood              | 1952    | amc | unreported  | 1 | 9  | N |

|         |           |                                                    |         |       |            |   |    |   |
|---------|-----------|----------------------------------------------------|---------|-------|------------|---|----|---|
|         |           |                                                    |         |       | d          |   |    |   |
| art_054 | raveel    | tuinmuurtje rood vierkant en het wit van de leegte | 1964    | amc   | unreported | 1 | 7  | N |
| art_055 | mulders   | zeeduivel                                          | 1998    | amc   | unreported | 1 | 7  | N |
| art_056 | lataster  | icarus atlanticus                                  | 1954    | amc   | unreported | 1 | 8  | N |
| art_057 | stuurman  | de busgarage                                       | 1993    | ing   | oil        | 1 | 5  | N |
| art_058 | van bohem | vrouwenfiguren                                     | 1979    | ing   | oil        | 1 | 9  | N |
| art_059 | stuurman  | delfshaven                                         | 1979    | ing   | oil        | 1 | 4  | N |
| art_060 | van bohem | macbeth                                            | 1976    | ing   | oil        | 1 | 8  | N |
| art_061 | stuurman  | de tramstraat                                      | 2003    | ing   | oil        | 1 | 6  | N |
| art_062 | molenkamp | pierrot                                            | 1978    | ing   | oil        | 1 | 5  | N |
| art_063 | molenkamp | de giraf                                           | 1988    | ing   | oil        | 1 | 6  | N |
| art_064 | van bohem | vegetatie groen blauw                              | 1974    | ing   | oil        | 1 | 8  | N |
| art_065 | stuurman  | de luchtbrug                                       | 1990    | ing   | oil        | 1 | 3  | N |
| art_066 | stuurman  | de meeuw                                           | 1994    | ing   | oil        | 1 | 4  | N |
| art_067 | van bohem | rugbyspeler                                        | 1967    | ing   | oil        | 1 | 20 | N |
| art_068 | corneille | l homme dans la ville                              | 1952    | cobra | unreported | 1 | 4  | N |
| art_069 | constant  | animaux                                            | 1949    | cobra | unreported | 1 | 3  | N |
| art_070 | rooskens  | paysage                                            | 1950    | cobra | unreported | 1 | 7  | N |
| art_071 | appel     | kleine jongen                                      | 1951    | cobra | unreported | 1 | 4  | N |
| art_072 | constant  | de parelvisser                                     | 1948    | cobra | unreported | 1 | 7  | N |
| art_073 | corneille | le grand oiseau                                    | 1951    | cobra | unreported | 1 | 2  | N |
| art_074 | constant  | personage de nuit                                  | 1948    | cobra | unreported | 1 | 3  | N |
| art_075 | pederson  | fruit of the heart                                 | 1957    | cobra | unreported | 1 | 3  | N |
| art_076 | jacobson  | untitled                                           | 1944    | cobra | unreported | 1 | 3  | N |
| art_077 | ortvad    | de haven                                           | 1949    | cobra | unreported | 1 | 3  | N |
| art_078 | jorn      | buketten                                           | 1947    | cobra | unreported | 1 | 3  | N |
| art_079 | appel     | twee figuren                                       | 1954    | cobra | unreported | 1 | 17 | N |
| art_080 | constant  | de stoel                                           | 1971    | cobra | unreported | 1 | 5  | N |
| art_081 | constant  | untitled                                           | 1956    | cobra | unreported | 1 | 3  | Y |
| art_082 | appel     | tetes fleuris                                      | 1961    | cobra | unreported | 1 | 3  | N |
| art_083 | miro      | painture III                                       | 1976    | cobra | unreported | 1 | 4  | N |
| art_084 | appel     | boy on a rocking horse                             | 1949    | cobra | unreported | 1 | 2  | N |
| art_085 | jorn      | unknown                                            | unknown | cobra | unreported | 1 | 2  | N |
| art_086 | corneille | le reine du                                        | 1968    | cobra | unreported | 1 | 3  | N |

|         |                 |                                    |      |       |             |   |   |   |
|---------|-----------------|------------------------------------|------|-------|-------------|---|---|---|
|         |                 | carnaval                           |      |       | d           |   |   |   |
| art_087 | hunziker        | schilderij nr 51                   | 1955 | cobra | unreported  | 1 | 3 | N |
| art_088 | corneille       | ville d ete                        | 1948 | cobra | unreported  | 1 | 3 | N |
| art_089 | corneille       | personage dans un paysage africain | 1950 | cobra | unreported  | 1 | 3 | N |
| art_090 | ortvad          | stiv kuling                        | 1947 | cobra | unreported  | 1 | 1 | N |
| art_091 | de jong         | playboy nr 1                       | 1964 | cobra | unreported  | 1 | 2 | N |
| art_092 | wagemaker       | untitled                           | 1968 | cobra | unreported  | 1 | 1 | N |
| art_093 | gribbling       | amimaux                            | 1949 | cobra | unreported  | 1 | 1 | N |
| art_094 | appel           | parende vogels                     | 1961 | cobra | unreported  | 1 | 3 | N |
| art_095 | wolvencamp      | untitled                           | 1970 | cobra | unreported  | 1 | 2 | N |
| art_096 | gear            | barred landscape                   | 1962 | cobra | unreported  | 1 | 2 | N |
| art_097 | appel           | paysage humain                     | 1958 | cobra | unreported  | 1 | 2 | N |
| art_098 | aleschinsky     | pas un mot                         | 1973 | cobra | unreported  | 1 | 2 | N |
| art_099 | jacobson        | demonic landscape                  | 1975 | cobra | unreported  | 1 | 3 | N |
| art_100 | verdijs         | A63                                | 1963 | cobra | unreported  | 1 | 2 | N |
| art_101 | pinot           | l arbero della vita                | 1960 | cobra | unreported  | 1 | 3 | N |
| art_102 | verdijs         | unknown                            | 1983 | cobra | acrylic     | 1 | 2 | N |
| art_103 | constant        | untitled                           | 1953 | gem   | spray paint | 1 | 9 | N |
| art_104 | schoonhoven     | relief 1970                        | 1970 | other | wall paint  | 1 | 2 | N |
| art_105 | schoonhoven     | postkantoor relief                 | 1958 | other | unknown     | 1 | 3 | N |
| art_106 | van der horst   | livia en augustus                  | 1995 | other | unreported  | 1 | 2 | N |
| art_107 | disseldorp      | mijnen                             | 1968 | other | unreported  | 1 | 2 | N |
| art_108 | smits           | untitled                           | 1983 | prins | acrylic     | 2 | 1 | N |
| art_109 | schoonhoven     | relief 81 13                       | 1981 | prins | latex       | 2 | 2 | N |
| art_110 | schoonhoven     | relief 70 54                       | 1970 | prins | latex       | 2 | 2 | N |
| art_111 | villevoye       | untitled                           | 1992 | prins | mixture     | 2 | 2 | N |
| art_112 | pape            | fontaine                           | 1981 | prins | oil         | 2 | 3 | N |
| art_113 | van merendonk   | untitled                           | 1987 | prins | oil         | 2 | 3 | N |
| art_114 | van der heijden | blauwe poort                       | 1984 | prins | oil         | 2 | 3 | N |
| art_115 | van der heijden | gebogen horizon                    | 1977 | prins | acrylic     | 2 | 3 | N |
| art_116 | bogart          | luchtweg                           | 1963 | prins | mixture     | 2 | 6 | N |
| art_117 | geurts          | untitled                           | 1987 | prins | oil         | 2 | 2 | N |
| art_118 | houtman         | untitled                           | 1989 | prins | acrylic     | 2 | 2 | N |
| art_119 | zwartjens       | brug                               | 1999 | prins | mix         | 2 | 2 | N |

|                |                 |                                          |         |       |             |   |   |   |
|----------------|-----------------|------------------------------------------|---------|-------|-------------|---|---|---|
| <b>art_120</b> | van oosten      | untitled                                 | unknown | prins | oil         | 2 | 4 | N |
| <b>art_121</b> | van oosten      | untitled                                 | unknown | prins | oil         | 2 | 3 | N |
| <b>art_122</b> | rijnders        | guillotine                               | 1964    | prins | unknown     | 2 | 4 | N |
| <b>art_123</b> | houbolt         | zicht op den haag                        | 1945    | prins | oil         | 2 | 2 | N |
| <b>art_124</b> | bogman          | zijlstraat te schiedam                   | 1925    | schie | unreported  | 2 | 1 | N |
| <b>art_125</b> | erfmann         | jongen met fiets                         | 1960    | schie | unreported  | 2 | 2 | N |
| <b>art_126</b> | armando         | peinture criminelle                      | 1957    | schie | unreported  | 2 | 2 | N |
| <b>art_127</b> | nieuwenhuijs    | slaapwandele<br>nde haan                 | 1949    | schie | unreported  | 2 | 5 | N |
| <b>art_128</b> | lucebert        | kale goeroe smelt berg                   | 1977    | schie | acrylic     | 2 | 4 | N |
| <b>art_129</b> | appel           | untitled                                 | 1961    | schie | unreported  | 2 | 2 | N |
| <b>art_130</b> | ouborg          | op zwarte vlek                           | 1930    | schie | unreported  | 2 | 2 | N |
| <b>art_131</b> | wolvencamp      | untitled                                 | 1961    | schie | unreported  | 2 | 2 | N |
| <b>art_132</b> | roede           | air breton                               | 1946    | schie | unreported  | 2 | 3 | N |
| <b>art_133</b> | rooskens        | compositie nr 2                          | 1954    | schie | unreported  | 2 | 3 | N |
| <b>art_134</b> | van golden      | two paintings                            | 1966    | schie | unreported  | 2 | 3 | N |
| <b>art_135</b> | verkade         | fastened sky                             | 1972    | schie | unreported  | 2 | 3 | N |
| <b>art_136</b> | hoekx           | voor e l                                 | 2010    | schie | mixture     | 2 | 2 | N |
| <b>art_137</b> | erfmann         | oosterse stad                            | 1938    | schie | unreported  | 2 | 2 | N |
| <b>art_138</b> | van der gaag    | attente supreme                          | 1970    | schie | unreported  | 2 | 2 | N |
| <b>art_139</b> | donia           | untitled                                 | 1997    | schie | gesso       | 2 | 2 | N |
| <b>art_140</b> | van golden      | celuy guy fut pris                       | 2006    | schie | unreported  | 2 | 2 | N |
| <b>art_141</b> | constant        | les touristes                            | 1972    | schie | unreported  | 2 | 2 | N |
| <b>art_142</b> | constant        | rwanda                                   | 1994    | schie | unreported  | 2 | 2 | N |
| <b>art_143</b> | cops            | dna streng                               | 2002    | schie | resin paint | 2 | 1 | N |
| <b>art_144</b> | hansen          | stuurloze vier                           | 1956    | schie | unreported  | 2 | 3 | N |
| <b>art_145</b> | content         | untitled                                 | 1985    | schie | unreported  | 2 | 2 | N |
| <b>art_146</b> | van elk         | portret van echtpaar piet en ida sanders | 1987    | schie | unreported  | 2 | 3 | N |
| <b>art_147</b> | van den ende    | wetmatige ordening weerspiegeling        | 2000    | schie | unreported  | 2 | 3 | N |
| <b>art_148</b> | raveel          | volk en bodem                            | 1961    | schie | unreported  | 2 | 2 | N |
| <b>art_149</b> | moss            | zwart en wit                             | 1932    | gem   | unreported  | 2 | 2 | N |
| <b>art_150</b> | jorn            | la rose feroce                           | 1961    | gem   | oil         | 2 | 3 | N |
| <b>art_151</b> | van der heijden | landloper                                | 1970    | gem   | unknown     | 2 | 2 | N |
| <b>art_152</b> | van der         | nr 35                                    | unknown | gem   | unknown     | 2 | 2 | N |

|         |                       |                               |         |       |            |     |   |   |
|---------|-----------------------|-------------------------------|---------|-------|------------|-----|---|---|
|         | heijden               |                               |         |       |            |     |   |   |
| art_153 | van der heijden       | wit op zwart                  | unknown | gem   | unknown    | 2   | 2 | N |
| art_154 | van der ploeg         | untitled                      | 2014    | gem   | acrylic    | 2   | 2 | N |
| art_155 | zandvliet             | rz 2013/09                    | 2013    | gem   | tempera    | 2   | 2 | N |
| art_156 | zandvliet             | rz 2013/07                    | 2013    | gem   | tempera    | 2   | 1 | N |
| art_157 | domela                | composition neo platique 5a   | 1924    | gem   | unreported | 2   | 2 | N |
| art_158 | van bart              | untitled                      | unknown | gem   | unreported | 2   | 1 | N |
| art_159 | van der haak          | madonna nr 8                  | 1984    | gem   | acrylic    | 2   | 1 | N |
| art_160 | de wint               | hollands zeegezicht           | 1972    | gem   | unreported | 2   | 2 | N |
| art_161 | van der leck          | de houthakkers                | 1928    | gem   | unreported | 2   | 1 | N |
| art_162 | van der leck          | compositie nr 1               | 1917    | gem   | unreported | 2   | 1 | N |
| art_163 | van der leck          | compositie nr 2               | 1917    | gem   | unreported | 2   | 1 | N |
| art_164 | de bie                | het verhaal van de zwaluw     | 1976    | gem   | unreported | 2   | 4 | N |
| art_165 | hansen                | uitjagers                     | 1958    | gem   | unreported | 2   | 2 | N |
| art_166 | dukker                | in de kamer                   | 1981    | gem   | unreported | 2   | 2 | N |
| art_167 | schuitema             | zelfportret 4                 | unknown | gem   | unreported | 2   | 3 | N |
| art_168 | schuitema             | zelfportret 5                 | unknown | gem   | unreported | 2   | 2 | N |
| art_169 | daniels               | queen skiing                  | 1987    | gem   | unreported | 2   | 2 | N |
| art_170 | constant              | erotic space                  | 1971    | gem   | unreported | 2   | 2 | N |
| art_171 | hussem                | bevrijding                    | 1954    | gem   | unreported | 2   | 3 | N |
| art_172 | rous                  | untitled                      | 1986    | gem   | unreported | 2   | 1 | N |
| art_173 | van golden            | untitled                      | 1988    | gem   | unreported | 2   | 2 | N |
| art_174 | de haan               | verfkoning                    | 1986    | gem   | unreported | 2   | 2 | N |
| art_175 | gogel                 | konzentration                 | 2005    | gem   | unreported | 2   | 2 | N |
| art_176 | van heemskerck        | bild no 109                   | 1920    | gem   | unreported | 2   | 1 | N |
| art_177 | de bie                | systeem van kleurenfotografie | 1986    | gem   | unreported | 2   | 1 | N |
| art_178 | birza                 | houten kip                    | 1988    | bfk   | tempera    |     | 0 | Y |
| art_179 | ryman                 | untitled                      | 1960    | other | oil        | 1   | 7 | Y |
| art_180 | schoonhoven           | schotelrelief                 | 1963    | rma   | unreported | n/a | 0 | Y |
| art_181 | victory boogie woogie | mondriaan                     | 1944    | gem   | oil        | n/a | 0 | Y |
| art_182 | kirchner              | der wald                      | 1925    | other | oil        | n/a | 0 | Y |
| art_183 | van gogh              | zonnenbloemen (retouch)       | n/a     | vgm   | unreported | n/a | 0 | Y |
| art_184 | van gogh              | field of irises near arles    | n/a     | vgm   | unreported | n/a | 0 | Y |

| (retouch)      |              |                                 |                      |       |         |     |   |   |
|----------------|--------------|---------------------------------|----------------------|-------|---------|-----|---|---|
| <b>art_185</b> | van bohemien | rode helm                       | unknown              | other | unknown | n/a | 0 | Y |
| <b>art_186</b> | rietveld     | leunstoel til brugman           | unknown (overpaint?) | Rma   | unknown | n/a | 0 | Y |
| <b>art_187</b> | bevort       | opvliegende eenden uit het riet | 1960                 | other | unknown | n/a | 0 | Y |
| <b>art_188</b> | hussum       | untitled                        | 1965                 | other | unknown | n/a | 0 | Y |
| <b>art_189</b> | unknown      | unknown                         | unknown              | rce   | oil     | 1   | 5 | Y |

*Bfk: Bouwfonds kunstcollectie, Cobra=Cobra museum Amstelveen, gem= gemeentemuseum den Haag, schie= Stedelijk Museum Schiedam, prins=Museum Prinsenhof Delft, rma= Rijksmuseum Amsterdam, vgm= van Gogh museum Amsterdam, AMC=AMC kunstcollectie, ING=ING kunstcollectie, rce= collection of the Cultural Heritage Agency of the Netherlands.*

- Instrument 1 = Bruker Tracer III-SD, 40 kV, 10µA, air, 10 s, no contact, Ti/Al filter.
- Instrument 2 = Bruker Tracer III-SD, 40kV, 15µA, air, 30 s, no contact, Ti/Al filter.

# Experimental– Reference dataset

Table S3 documents the reference dataset.

*Table S3: Reference dataset*

| Artwork_id | Time/year    | description                                | Binding medium    |
|------------|--------------|--------------------------------------------|-------------------|
| ref_001    | contemporary | Uncoated anatase, PVC=15%, 50 um           | oil               |
| ref_002    | contemporary | Uncoated anatase, PVC=15%, 100 um          | oil               |
| ref_003    | contemporary | Uncoated anatase, PVC=15%, 150 um, UV aged | oil               |
| ref_004    | contemporary | Uncoated anatase, PVC=15%, 200 um          | oil               |
| ref_005    | contemporary | Uncoated anatase, PVC=5%                   | oil               |
| ref_006    | contemporary | Uncoated anatase, PVC=8%                   | oil               |
| ref_007    | contemporary | Uncoated anatase, PVC=10%                  | oil               |
| ref_008    | contemporary | Uncoated anatase, PVC=25%                  | oil               |
| ref_009    | contemporary | Coated rutile, PVC=15%                     | oil               |
| ref_010    | contemporary | Coated rutile, PVC=35%                     | oil               |
| ref_011    | unknown      | TiO2<br>RCE9705, Kronos CL300              | oil               |
| ref_012    | unknown      | TiO2<br>RCE9617, Tiofine A                 | oil               |
| ref_013    | unknown      | TiO2<br>RCE9611, R900                      | oil               |
| ref_014    | unknown      | TiO2<br>RCE9649, Sikkens                   | oil               |
| ref_015    | unknown      | TiO2<br>RCE1924                            | oil               |
| ref_016    | unknown      | TiO2<br>RCE2766                            | oil               |
| ref_017    | contemporary | Cobra +++105 tube                          | watermiscible oil |
| ref_018    | contemporary | Cobra +++106<br>Tube                       | watermiscible oil |
| ref_019    | contemporary | Rembrandt serie 1+++118 tube               | oil               |
| ref_020    | contemporary | Rembrandt serie 1+++105 tube               | oil               |
| ref_021    | contemporary | W&N artisan tube                           | oil               |
| ref_022    | contemporary | W&N Artist colour tube                     | oil               |
| ref_023    | contemporary | TiO2 (verfmolen de kat)                    | oil               |
| ref_024    | contemporary | TiO2 Pavercolor                            | oil               |
| ref_025    | unknown      | ZnO (JS)                                   | oil               |
| ref_026    | unknown      | ZnO (JS) + TiO2 RCE9617                    | oil               |
| ref_027    | contemporary | CaCO3 (kremer)                             | oil               |
| ref_028    | contemporary | Winton tube                                | oil               |
| ref_029    | contemporary | TiO2 Hombitan LO-CR-K                      | oil               |
| ref_030    | contemporary | TiO2 + ZnO (kremer), 0.1:0.09 v/v          | oil               |
| ref_031    | contemporary | TiO2 + ZnO (kremer), 0.05:0.09 v/v         | oil               |
| ref_032    | contemporary | TiO2 + ZnO (kremer), 0.06:0.06 v/v         | oil               |

|         |              |                                                                                                     |     |
|---------|--------------|-----------------------------------------------------------------------------------------------------|-----|
| ref_033 | contemporary | TiO <sub>2</sub> + ZnO (kremer), 0.11:0.08 v/v                                                      | oil |
| ref_034 | contemporary | ZnO (kremer)                                                                                        | oil |
| ref_035 | contemporary | ZnO (kremer)                                                                                        | oil |
| ref_036 | contemporary | TiO <sub>2</sub> + ZnO (kremer), 0.05:0.05 v/v                                                      | oil |
| ref_037 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer)+<br>BaSO <sub>4</sub> (kremer), 0.14:0.05, 0.05 v/v/v | oil |
| ref_038 | contemporary | Uncoated anatase + BaSO <sub>4</sub> (kremer), 0.14:<br>0.13 v/v, thick layer                       | oil |
| ref_039 | contemporary | Uncoated anatase + BaSO <sub>4</sub> (kremer), 0.14:<br>0.13 v/v, thin layer                        | oil |
| ref_040 | contemporary | Uncoated anatase + BaSO <sub>4</sub> (kremer), 0.14:<br>0.13 v/v                                    | oil |
| ref_041 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer), 0.14:<br>0.13 v/v                                    | oil |
| ref_042 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer), 0.14:<br>0.07 v/v                                    | oil |
| ref_043 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer)+<br>BaSO <sub>4</sub> (kremer), 0.14:0.03, 0.01 v/v/v | oil |
| ref_044 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer)+<br>BaSO <sub>4</sub> (kremer), 0.14:0.06, 0.08 v/v/v | oil |
| ref_045 | contemporary | Uncoated anatase + BaSO <sub>4</sub> (kremer), 0.14:<br>0.04 v/v                                    | oil |
| ref_046 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer)+<br>BaSO <sub>4</sub> (kremer), 0.14:0.09, 0.04 v/v/v | oil |
| ref_047 | contemporary | Uncoated anatase + CaCO <sub>3</sub> (kremer)+<br>BaSO <sub>4</sub> (kremer), 0.14:0.03, 0.08 v/v/v | oil |
| ref_048 | contemporary | BaSO <sub>4</sub> (kremer)                                                                          | oil |
| ref_049 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer) (1:99,<br>v/v)                                         | oil |
| ref_050 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer) (5:95,<br>v/v)                                         | oil |
| ref_051 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer)<br>(10:90, v/v)                                        | oil |
| ref_052 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer)<br>(25:75, v/v)                                        | oil |
| ref_053 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer)<br>(50:50, v/v)                                        | oil |
| ref_054 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer)<br>(75:25, v/v)                                        | oil |
| ref_055 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer)<br>(90:10, v/v)                                        | oil |
| ref_056 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer) (95:5,<br>v/v)                                         | oil |
| ref_057 | contemporary | Uncoated anatase +BaSO <sub>4</sub> (kremer) (99:1,<br>v/v)                                         | oil |
| ref_058 | contemporary | Uncoated anatase                                                                                    | oil |
| ref_059 | contemporary | Coated rutile                                                                                       | oil |
| ref_060 | contemporary | TiO <sub>2</sub> , Huntsman HD CD                                                                   | oil |
| ref_061 | contemporary | TiO <sub>2</sub> , Hunstman A-PP2                                                                   | oil |
| ref_062 | contemporary | TiO <sub>2</sub> , Hunstman A-HRF                                                                   | oil |
| ref_063 | contemporary | Prepered canvas(1)                                                                                  | oil |
| ref_064 | contemporary | Canvas(1) + uncoated anatase, thick layer                                                           | oil |
| ref_065 | contemporary | Canvas(1) + uncoated anatase, thin layer                                                            | oil |
| ref_066 | contemporary | Canvas(1) + coated rutile, thick layer                                                              | oil |
| ref_067 | contemporary | Canvas(1) + coated rutile, thin layer                                                               | oil |
| ref_068 | contemporary | Canvas(1) + ZnO (kremer), thick layer                                                               | oil |
| ref_069 | contemporary | Canvas(1) + ZnO (kremer), thin layer                                                                | oil |

|         |              |                                                                                   |     |
|---------|--------------|-----------------------------------------------------------------------------------|-----|
| ref_070 | contemporary | Canvas(1) + BaSO4 (kremer), thick layer                                           | oil |
| ref_071 | contemporary | Canvas(1) + BaSO4 (kremer), thin layer                                            | oil |
| ref_072 | contemporary | Canvas(1) + CaCO3 (kremer), thick layer                                           | oil |
| ref_073 | contemporary | Canvas(1) + CaCO3 (kremer), thin layer                                            | oil |
| ref_074 | contemporary | Canvas(1) + Uncoated anatase mixed with aluminum stearate, thick layer            | oil |
| ref_075 | contemporary | Canvas(1) + Uncoated anatase mixed with aluminum stearate, thin layer             | oil |
| ref_076 | contemporary | Canvas(1) + Uncoated anatase mixed with ZnO (kremer), thick layer                 | oil |
| ref_077 | contemporary | Canvas(1) + Uncoated anatase mixed with ZnO (kremer), thin layer                  | oil |
| ref_078 | contemporary | Canvas(1) + Uncoated anatase mixed with BaSO4 (kremer), thick layer               | oil |
| ref_079 | contemporary | Canvas(1) + Uncoated anatase mixed with BaSO4 (kremer), thin layer                | oil |
| ref_080 | contemporary | Canvas(1) + Uncoated anatase mixed with CaCO3 (kremer), thick layer               | oil |
| ref_081 | contemporary | Canvas(1) + Uncoated anatase mixed with CaCO3 (kremer), thin layer                | oil |
| ref_082 | 1982         | Canvas(1) + Amsterdam Oil colours Tube                                            | oil |
| ref_083 | contemporary | Canvas(1) + Talens van Gogh oil paint tube                                        | oil |
| ref_084 | mix          | Canvas(1) + Uncoated anatase + Talens Amsterdam Oil colours tube, thick layer     | oil |
| ref_085 | mix          | Canvas(1) + Uncoated anatase + Talens Amsterdam Oil colours tube, thin layer      | oil |
| ref_086 | contemporary | Canvas(1) + Uncoated anatase + Talens van Gogh oil paint tube, thick layer        | oil |
| ref_087 | contemporary | Canvas(1) + Uncoated anatase + Talens van Gogh oil paint tube, thin layer         | oil |
| ref_088 | mix          | Canvas(1) + Uncoated anatase/ZnO + Talens Amsterdam Oil colours tube, thick layer | oil |
| ref_089 | mix          | Canvas(1) + Uncoated anatase/ZnO + Talens Amsterdam Oil colours tube, thin layer  | oil |
| ref_090 | contemporary | Canvas(1) + Uncoated anatase/ZnO + Talens van Gogh oil paint tube, thick layer    | oil |
| ref_091 | contemporary | Canvas(1) + Uncoated anatase/ ZnO + Talens van Gogh oil paint tube, thin layer    | oil |
| ref_092 | contemporary | Lead white 200 um                                                                 | oil |
| ref_093 | contemporary | Lead white + uncoated anatase, thick layer                                        | oil |
| ref_094 | contemporary | Lead white + uncoated anatase, thin layer                                         | oil |
| ref_095 | contemporary | Lead white + ZnO (kremer), thick layer                                            | oil |
| ref_096 | contemporary | Lead white + ZnO (kremer), thick layer                                            | oil |
| ref_097 | contemporary | TiO2 + lead white, thick layer                                                    | oil |
| ref_098 | contemporary | TiO2 + lead white, thin layer                                                     | oil |
| ref_099 | contemporary | TiO2 + ZnO(kremer), thick layer                                                   | oil |
| ref_100 | contemporary | TiO2 + ZnO (kremer), thin layer                                                   | oil |
| ref_101 | contemporary | ZnO(kremer) + lead white, thick layer                                             | oil |
| ref_102 | contemporary | ZnO(kremer) + lead white, thin layer                                              | oil |
| ref_103 | contemporary | ZnO (kremer) + uncoated anatase, thick layer                                      | oil |
| ref_104 | contemporary | ZnO (kremer) + uncoated anatase, thin layer.                                      | oil |
| ref_105 | unknown      | RCE10138, tube                                                                    | oil |

|         |              |                                                                  |         |
|---------|--------------|------------------------------------------------------------------|---------|
| ref_106 | unknown      | TiO <sub>2</sub> ,<br>RCE2763                                    | oil     |
| ref_107 | unknown      | RCE9711, tube                                                    | oil     |
| ref_108 | unknown      | RCE9733, tube                                                    | oil     |
| ref_109 | unknown      | Titaanwit, old holland oil colours, tube,<br>thick layer         | oil     |
| ref_110 | unknown      | Titaanwit, old holland oil colours, tube,<br>thin layer          | oil     |
| ref_111 | unknown      | Tiofine                                                          | oil     |
| ref_112 | 1944         | W&N powder 3915 10-10-44                                         | oil     |
| ref_113 | 1941         | W&N powder 3557 30-5-41                                          | oil     |
| ref_114 | 1941         | W&N powder 963 10-6-41                                           | oil     |
| ref_115 | 1941         | W&N powder 3914 10-10-41                                         | oil     |
| ref_116 | contemporary | Prepared canvas(2)                                               | ground  |
| ref_117 | contemporary | Canvas(2) + Soft body liquitex paint                             | acrylic |
| ref_118 | contemporary | Canvas(2) + Soft body liquitex paint mixed<br>with coated rutile | acrylic |
| ref_119 | contemporary | Canvas(2) + Gamblin oil colours                                  | Oil     |
| ref_120 | 1982         | Talens, amsterdam oil colours tube.                              | oil     |
| ref_121 | unknown      | LUCAS designer Gouache tube 8007                                 | gouache |
| ref_122 | contemporary | Action van Bleiswijk Holland Acrylic tube                        | acrylic |
| ref_123 | contemporary | W&N Gouache tube                                                 | gouache |
| ref_124 | unknown      | Greyhound Reeved oil color tube                                  | oil     |
| ref_125 | contemporary | Lascaux Gouache tube                                             | gouache |
| ref_126 | 1975         | Talens, van Gogh oil colors tube                                 | oil     |
| ref_127 | 1999         | Block titaan wit tube                                            | oil     |
| ref_128 | unknown      | Egg tempera tube                                                 | tempera |
| ref_129 | 1963         | W&N Swatch 1963                                                  | oil     |
| ref_130 | 1968         | W&N Swatch 1968                                                  | oil     |
| ref_131 | 1972         | W&N Swatch 1972                                                  | oil     |
| ref_132 | 1987         | W&N Swatch 1987                                                  | oil     |
| ref_133 | 1964         | W&N Swatch 1964                                                  | oil     |
| ref_134 | contemporary | BaSO <sub>4</sub> + ZnO (kremer), thick layer                    | oil     |
| ref_135 | contemporary | BaSO <sub>4</sub> + ZnO (kremer), thin layer                     | oil     |
| ref_136 | contemporary | BaSO <sub>4</sub> (kremer) + uncoated anatase , thick<br>layer   | oil     |
| ref_137 | contemporary | BaSO <sub>4</sub> (kremer) + uncoated anatase , thin<br>layer    | oil     |
| ref_138 | contemporary | CaCO <sub>3</sub> + ZnO (kremer), thick layer                    | oil     |
| ref_139 | contemporary | CaCO <sub>3</sub> + ZnO (kremer), thin layer                     | oil     |
| ref_140 | contemporary | CaCO <sub>3</sub> (kremer) + uncoated anatase , thick<br>layer   | oil     |
| ref_141 | contemporary | CaCO <sub>3</sub> (kremer) + uncoated anatase , thin<br>layer    | oil     |
| ref_142 | 2012         | Uncoated anatase                                                 | none    |
| ref_143 | 2012         | Coated rutile                                                    | none    |
| ref_144 | unknown      | Lukas 2488                                                       | none    |
| ref_145 | 2015         | Talens Gouache tube                                              | gouache |
| ref_146 | 1943         | W&NTube_TiWhite_197/8_16-7-43_03 &<br>_04                        | oil     |
| ref_147 | 1946         | W&NTube_TiWhite_93/04Mill_22-6-46:                               | oil     |

|         |         |                                                         |         |
|---------|---------|---------------------------------------------------------|---------|
|         |         | _03 & _04                                               |         |
| ref_148 | 1947    | W&NTube_TiWhite_197/8Mill_19-9-47:<br>_01 & _02         | oil     |
| ref_149 | 1956    | W&NTube_Student_TiWhite_687_22-4-<br>56: _07 & 08       | oil     |
| ref_150 | 1958    | W&NTube_Students_TiWhite_687_15-10-<br>58: _05 & 06     | oil     |
| ref_151 | 1959    | W&NTube_TiWhite_687_22-10-59: _01 &<br>_02              | oil     |
| ref_152 | 1963    | W&NTube_Students_TiWhite_Mill742_30-<br>4-63: _01 & _02 | oil     |
| ref_153 | 1990    | Smincke gouache tube                                    | gouache |
| ref_154 | 2012    | Deckweiss tube                                          | unknown |
| ref_155 | 1995    | Finity tube                                             | acrylic |
| ref_156 | unknown | Egg tempera tube.                                       | tempera |

*All references were taped to a Perspex backing board and analysed with instrument 2.*

Table S4 documents useful information for the interpretation of Table S3.

**Table S4: Useful abbreviations, comments and codes for the reference dataset**

| Name/code/abbreviation             | Comment                                                                                                 |
|------------------------------------|---------------------------------------------------------------------------------------------------------|
| RCE###                             | Code from reference collection cultural heritage agency of the Netherlands                              |
| # um                               | Layers thickness, if not specified: 100 micron                                                          |
| %                                  | Pigment volume concentration                                                                            |
| /                                  | Mixtures                                                                                                |
| +                                  | Layers                                                                                                  |
| W&N powder                         | Winsor&Newton powder from archive                                                                       |
| W&N swatch                         | Winsor&Newton paint out made per year (from archive)                                                    |
| W&N tube                           | Winsor&Newton small test tubes from archive                                                             |
| Uncoated anatase                   | Hombitan LW                                                                                             |
| Coated rutile                      | Tronox CR-826                                                                                           |
| 'tube'                             | All tubes were sold as 'titanium white'                                                                 |
| Not tuber (self-made paint)        | All non-tubes were prepared with van Beek bleached linseed oil and a drier (mix on a glass-plated mill) |
| JS                                 | Joop Schoonman collection                                                                               |
| Kremer                             | Kremer Pigmente, where ZnO, BaSO <sub>4</sub> , CaCO <sub>3</sub> and aluminium stearate were purchased |
| Huntman/ Finity/Tiofine and others | Brand names/ labels on jars etc.                                                                        |
| Thin/Thick layer                   | Manually applied by brush, not measured.                                                                |

# Using the Al/Ti filter

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Figure S1 indicates spectral changes occurring due to the Al/Ti filter.

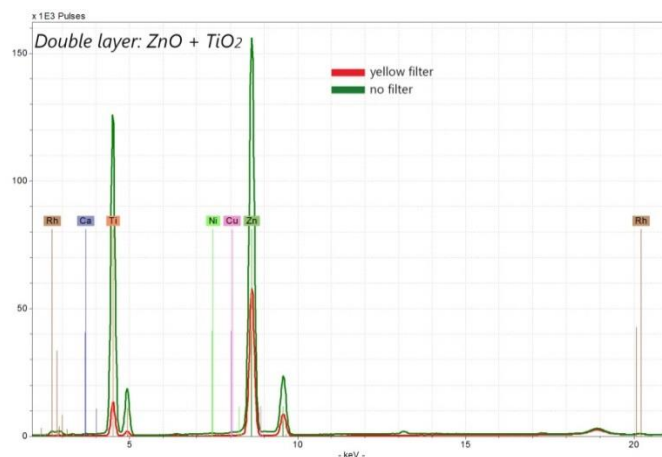
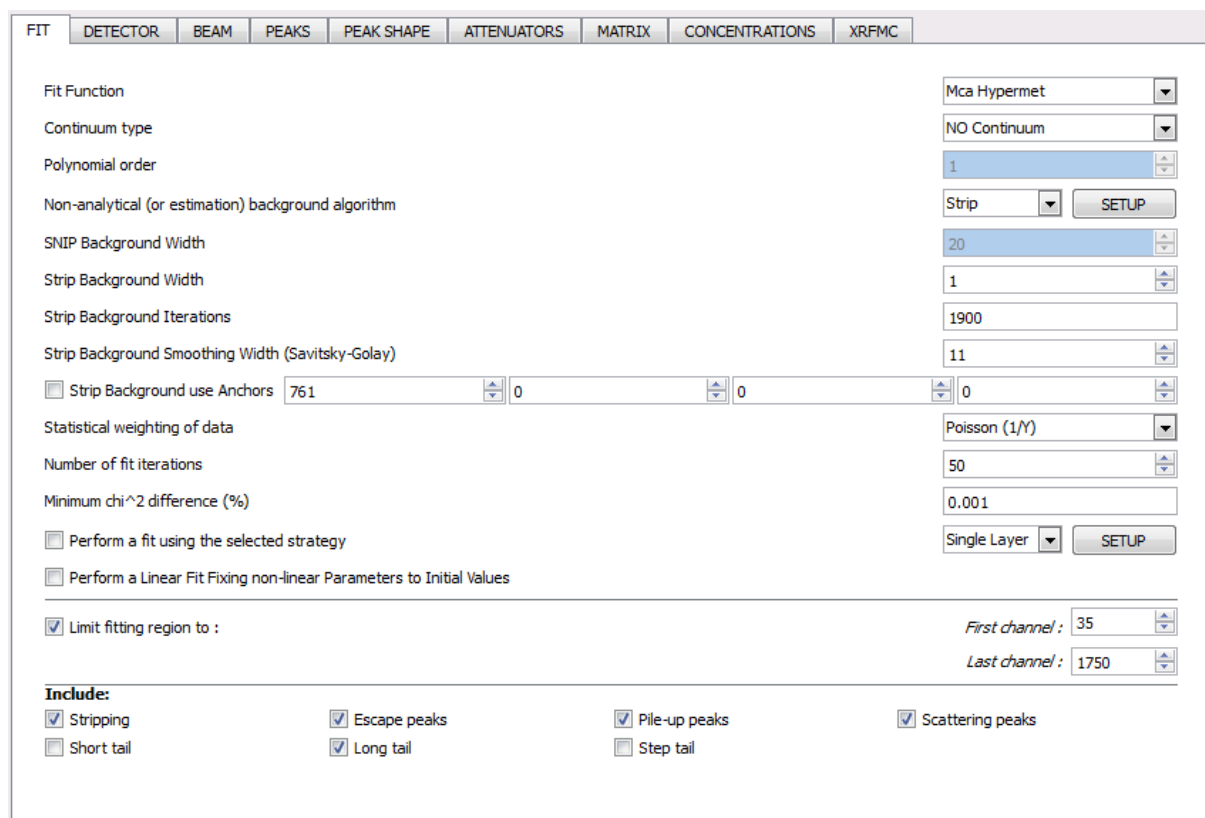


**Figure S1: Spectrum of a double layer system containing a layer zinc white under a layer of titanium dioxide, measured with and without the yellow filter.**

# Experimental– PyMCA deconvolution.

Figure S2 until Figure S10 show the PyMCA deconvolution settings (PyMCA is a free software). This deconvolution configuration can be used to deconvolute spectra of modern paintings taken with a Bruker III-SD XRF spectrophotometer using the Ti/Al filter.



The image shows the 'FIT' tab of the PyMCA software interface. It contains various settings for the deconvolution process, including fit function, background algorithm, statistical weighting, and fitting region limits.

**Fit Function:** Mca Hypermet

**Continuum type:** NO Continuum

**Polynomial order:** 1

**Non-analytical (or estimation) background algorithm:** Strip

**SNIP Background Width:** 20

**Strip Background Width:** 1

**Strip Background Iterations:** 1900

**Strip Background Smoothing Width (Savitsky-Golay):** 11

**Strip Background use Anchors:** 761, 0, 0, 0

**Statistical weighting of data:** Poisson (1/Y)

**Number of fit iterations:** 50

**Minimum  $\chi^2$  difference (%):** 0.001

**Perform a fit using the selected strategy:** ☐

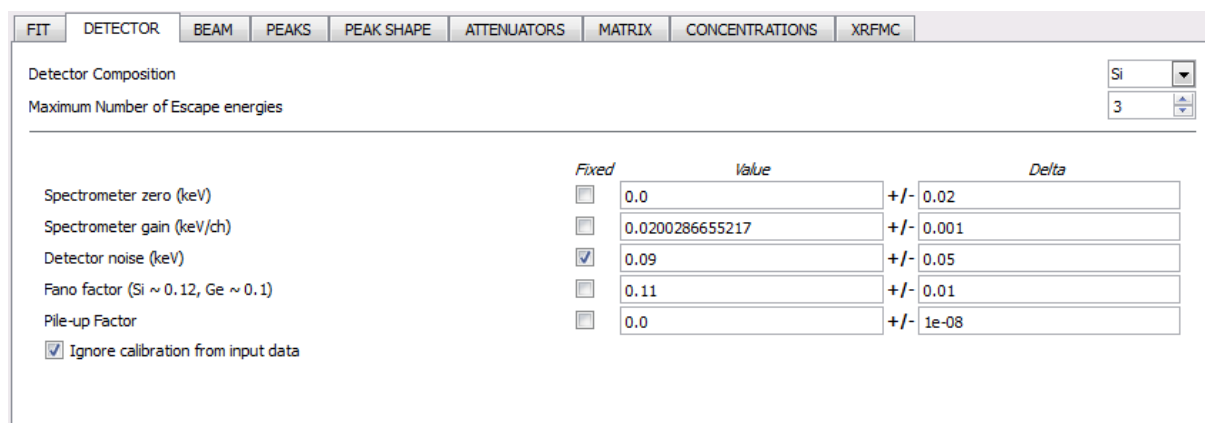
**Perform a Linear Fit Fixing non-linear Parameters to Initial Values:** ☐

**Limit fitting region to:** ☒ First channel: 35, Last channel: 1750

**Include:**

- ☒ Stripping
- ☒ Escape peaks
- ☒ Pile-up peaks
- ☒ Scattering peaks
- ☐ Short tail
- ☒ Long tail
- ☐ Step tail

Figure S2: Fit parameters PyMCA



The image shows the 'DETECTOR' tab of the PyMCA software interface. It contains settings for detector composition, maximum number of escape energies, and a table of fixed and variable parameters with their values and uncertainties.

**Detector Composition:** Si

**Maximum Number of Escape energies:** 3

|                                   | Fixed                               | Value           | +/- | Delta |
|-----------------------------------|-------------------------------------|-----------------|-----|-------|
| Spectrometer zero (keV)           | <input type="checkbox"/>            | 0.0             | +/- | 0.02  |
| Spectrometer gain (keV/ch)        | <input type="checkbox"/>            | 0.0200286655217 | +/- | 0.001 |
| Detector noise (keV)              | <input checked="" type="checkbox"/> | 0.09            | +/- | 0.05  |
| Fano factor (Si ~ 0.12, Ge ~ 0.1) | <input type="checkbox"/>            | 0.11            | +/- | 0.01  |
| Pile-up Factor                    | <input type="checkbox"/>            | 0.0             | +/- | 1e-08 |

**Ignore calibration from input data:** ☒

Figure S3: Detector parameters PyMCA

| FIT                                           | DETECTOR  | BEAM         | PEAKS                                         | PEAK SHAPE | ATTENUATORS | MATRIX                                        | CONCENTRATIONS | XRFMC       |                                               |
|-----------------------------------------------|-----------|--------------|-----------------------------------------------|------------|-------------|-----------------------------------------------|----------------|-------------|-----------------------------------------------|
| Open X-Ray Tube Setup                         |           |              |                                               |            |             |                                               |                |             |                                               |
| Use                                           | Energy    | Weight       | Use                                           | Energy     | Weight      | Use                                           | Energy         | Weight      | Use                                           |
| <input checked="" type="checkbox"/> Energy 0  | 20.073800 | 10024.955794 | <input checked="" type="checkbox"/> Energy 20 | 4.600000   | 2855.141891 | <input checked="" type="checkbox"/> Energy 40 | 8.600000       | 4113.538284 | <input checked="" type="checkbox"/> Energy 60 |
| <input checked="" type="checkbox"/> Energy 1  | 20.216100 | 18999.742818 | <input checked="" type="checkbox"/> Energy 21 | 4.800000   | 3109.536862 | <input checked="" type="checkbox"/> Energy 41 | 8.800000       | 4064.436562 | <input checked="" type="checkbox"/> Energy 61 |
| <input checked="" type="checkbox"/> Energy 2  | 22.698900 | 1739.059534  | <input checked="" type="checkbox"/> Energy 22 | 5.000000   | 3336.865493 | <input checked="" type="checkbox"/> Energy 42 | 9.000000       | 4012.448908 | <input checked="" type="checkbox"/> Energy 62 |
| <input checked="" type="checkbox"/> Energy 3  | 22.723700 | 3388.440853  | <input checked="" type="checkbox"/> Energy 23 | 5.200000   | 3539.997418 | <input checked="" type="checkbox"/> Energy 43 | 9.200000       | 3958.125908 | <input checked="" type="checkbox"/> Energy 63 |
| <input checked="" type="checkbox"/> Energy 4  | 1.400000  | 14.771225    | <input checked="" type="checkbox"/> Energy 24 | 5.400000   | 3715.112412 | <input checked="" type="checkbox"/> Energy 44 | 9.400000       | 3901.946470 | <input checked="" type="checkbox"/> Energy 64 |
| <input checked="" type="checkbox"/> Energy 5  | 1.600000  | 116.920790   | <input checked="" type="checkbox"/> Energy 25 | 5.600000   | 3863.232521 | <input checked="" type="checkbox"/> Energy 45 | 9.600000       | 3844.326230 | <input checked="" type="checkbox"/> Energy 65 |
| <input checked="" type="checkbox"/> Energy 6  | 1.800000  | 439.929574   | <input checked="" type="checkbox"/> Energy 26 | 5.800000   | 3985.926723 | <input checked="" type="checkbox"/> Energy 46 | 9.800000       | 3785.625125 | <input checked="" type="checkbox"/> Energy 66 |
| <input checked="" type="checkbox"/> Energy 7  | 2.000000  | 1054.811760  | <input checked="" type="checkbox"/> Energy 27 | 6.000000   | 4085.093318 | <input checked="" type="checkbox"/> Energy 47 | 10.000000      | 3726.154175 | <input checked="" type="checkbox"/> Energy 67 |
| <input checked="" type="checkbox"/> Energy 8  | 2.200000  | 1948.099394  | <input checked="" type="checkbox"/> Energy 28 | 6.200000   | 4167.636773 | <input checked="" type="checkbox"/> Energy 48 | 10.200000      | 3666.837725 | <input checked="" type="checkbox"/> Energy 68 |
| <input checked="" type="checkbox"/> Energy 9  | 2.400000  | 2982.581403  | <input checked="" type="checkbox"/> Energy 29 | 6.400000   | 4230.106042 | <input checked="" type="checkbox"/> Energy 49 | 10.400000      | 3607.156565 | <input checked="" type="checkbox"/> Energy 69 |
| <input checked="" type="checkbox"/> Energy 10 | 2.600000  | 4027.315040  | <input checked="" type="checkbox"/> Energy 30 | 6.600000   | 4274.621071 | <input checked="" type="checkbox"/> Energy 50 | 10.600000      | 3547.319924 | <input checked="" type="checkbox"/> Energy 70 |
| <input checked="" type="checkbox"/> Energy 11 | 2.800000  | 4987.004775  | <input checked="" type="checkbox"/> Energy 31 | 6.800000   | 4303.215295 | <input checked="" type="checkbox"/> Energy 51 | 10.800000      | 3487.507010 | <input checked="" type="checkbox"/> Energy 71 |
| <input checked="" type="checkbox"/> Energy 12 | 3.000000  | 5809.568329  | <input checked="" type="checkbox"/> Energy 32 | 7.000000   | 4317.796888 | <input checked="" type="checkbox"/> Energy 52 | 11.000000      | 3427.870822 | <input checked="" type="checkbox"/> Energy 72 |
| <input checked="" type="checkbox"/> Energy 13 | 3.200000  | 1045.789280  | <input checked="" type="checkbox"/> Energy 33 | 7.200000   | 4320.127398 | <input checked="" type="checkbox"/> Energy 53 | 11.200000      | 3368.541492 | <input checked="" type="checkbox"/> Energy 73 |
| <input checked="" type="checkbox"/> Energy 14 | 3.400000  | 1369.218339  | <input checked="" type="checkbox"/> Energy 34 | 7.400000   | 4311.812724 | <input checked="" type="checkbox"/> Energy 54 | 11.400000      | 3309.629219 | <input checked="" type="checkbox"/> Energy 74 |
| <input checked="" type="checkbox"/> Energy 15 | 3.600000  | 1353.534898  | <input checked="" type="checkbox"/> Energy 35 | 7.600000   | 4294.302568 | <input checked="" type="checkbox"/> Energy 55 | 11.600000      | 3251.226844 | <input checked="" type="checkbox"/> Energy 75 |
| <input checked="" type="checkbox"/> Energy 16 | 3.800000  | 1657.013262  | <input checked="" type="checkbox"/> Energy 36 | 7.800000   | 4268.895451 | <input checked="" type="checkbox"/> Energy 56 | 11.800000      | 3193.412099 | <input checked="" type="checkbox"/> Energy 76 |
| <input checked="" type="checkbox"/> Energy 17 | 4.000000  | 1961.305940  | <input checked="" type="checkbox"/> Energy 37 | 8.000000   | 4236.747185 | <input checked="" type="checkbox"/> Energy 57 | 12.000000      | 3136.249574 | <input checked="" type="checkbox"/> Energy 77 |
| <input checked="" type="checkbox"/> Energy 18 | 4.200000  | 2275.967975  | <input checked="" type="checkbox"/> Energy 38 | 8.200000   | 4200.466935 | <input checked="" type="checkbox"/> Energy 58 | 12.200000      | 3079.792443 | <input checked="" type="checkbox"/> Energy 78 |
| <input checked="" type="checkbox"/> Energy 19 | 4.400000  | 2575.939979  | <input checked="" type="checkbox"/> Energy 39 | 8.400000   | 4159.122569 | <input checked="" type="checkbox"/> Energy 59 | 12.400000      | 3024.083966 | <input checked="" type="checkbox"/> Energy 79 |

Figure S4: Beam parameters PyMCA, checked up to Energy 137.

| FIT | DETECTOR | BEAM | PEAKS | PEAK SHAPE | ATTENUATORS | MATRIX | CONCENTRATIONS | XRFMC |
|-----|----------|------|-------|------------|-------------|--------|----------------|-------|
|-----|----------|------|-------|------------|-------------|--------|----------------|-------|

Excitation Energy (keV)

39.7000

H

Li

Be

Na

Mg

K

Ca

Sc

Ti

V

Cr

Mn

Fe

Co

Ni

Cu

Zn

Ga

Ge

As

Se

Br

Kr

Rb

Sr

Y

Zr

Nb

Mo

Tc

Ru

Rh

Pd

Ag

Cd

In

Sn

Sb

Te

I

Xe

Cs

Ba

La

Hf

Ta

W

Re

Os

Ir

Pt

Au

Hg

Tl

Pb

Bi

Po

At

Rn

Fr

Ra

Ac

Rf

Db

Sg

Bh

Hs

Mt

He

B

C

N

O

F

Ne

Al

Si

P

S

Cl

Ar

Ce

Pr

Nd

Pm

Sm

Eu

Gd

Tb

Dy

Ho

Er

Tm

Yb

Lu

Th

Pa

U

Np

Pu

Am

Cm

Bk

Cf

Es

Fm

Md

No

Lr

K

Ka

Kb

L

L1

L2

L3

M

Reset

Reset All

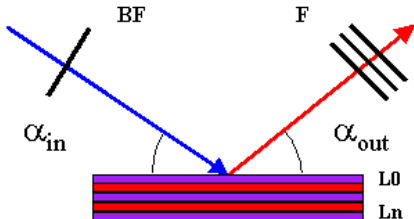
Figure S5: Selected peaks PyMCA

**Figure S6: Peak shape parameters PyMCA**

**Figure S7: Attenuator parameters PyMCA**

| FIT | DETECTOR | BEAM | PEAKS | PEAK SHAPE | ATTENUATORS | MATRIX | CONCENTRATIONS | XRFMC |
|-----|----------|------|-------|------------|-------------|--------|----------------|-------|
|-----|----------|------|-------|------------|-------------|--------|----------------|-------|



Incoming Angle (deg.):

Outgoing Angle (deg.):

☒ Scattering Angle (deg.):

This matrix definition will only be considered if Matrix is selected and material is set to MULTILAYER in the ATTENUATORS tab.

| Layer                           | Name   | Material   | Density (g/cm3) | Thickness (cm) |
|---------------------------------|--------|------------|-----------------|----------------|
| <input type="checkbox"/> Layer0 | Layer0 | Artax_Sn48 | 4.86e-05        | 1.0            |
| <input type="checkbox"/> Layer1 | Layer1 | Arlen_Zr   | 6.53            | 0.025          |
| <input type="checkbox"/> Layer2 | Layer2 | Arlen_Zn   | 7.14            | 0.0254         |
| <input type="checkbox"/> Layer3 | Layer3 | Arlen_Co   | 8.9             | 0.005          |
| <input type="checkbox"/> Layer4 | Layer4 | Arlen_Ag   | 6.691           | 0.003          |
| <input type="checkbox"/> Layer5 | Layer5 | Arlen_Mo   | 10.22           | 0.0025         |
| <input type="checkbox"/> Layer6 | Layer6 | Arlen_Pb   | 11.34           | 0.0152         |
| <input type="checkbox"/> Layer7 | Layer7 | Arlen_Ti   | 4.54            | 0.00125        |
| <input type="checkbox"/> Layer8 | Layer8 | Cu         | 8.94            | 0.1            |
| <input type="checkbox"/> Layer9 | Layer9 | Mylar      | 1.4             | 0.00025        |

Figure S8: Matrix parameters PyMCA

| FIT | DETECTOR | BEAM | PEAKS | PEAK SHAPE | ATTENUATORS | MATRIX | CONCENTRATIONS | XRFMC |
|-----|----------|------|-------|------------|-------------|--------|----------------|-------|
|-----|----------|------|-------|------------|-------------|--------|----------------|-------|

☒ From fundamental parameters

Flux (photons/s)

Active Area (cm2)

x time(seconds)

distance (cm)

☒ Use Automatic Factor

☐ From matrix composition

Matrix Reference Element: Auto

☒ Consider attenuators in calculations

☐ Consider secondary excitation

☐ Consider tertiary excitation

☐ use Monte Carlo code to correct higher order excitations

☐ Elemental mM concentrations (assuming 1 l of solution is 1000 \* matrix\_density grams)

Figure S9: Concentrations PyMCA

| FIT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | DETECTOR  | BEAM                                                                 | PEAKS | PEAK SHAPE | ATTENUATORS | MATRIX | CONCENTRATIONS | XRFMC |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|----------------------------------------------------------------------|-------|------------|-------------|--------|----------------|-------|----------------------------------|---------|----------------------------------------------------------------------|-----------------------------------|---------|----------------------------------------------------------------------|---------------------------------|---------|----------------------------------------------------------------------|-------------------------------------|---------|----------------------------------------------------------------------|-----------------------------------|---------|----------------------------------------------------------------------|-------------------------------------|-----------|----------------------------------------------------------------------|--------------------------------------|-----------|----------------------------------------------------------------------|------------------|---------|----------------------------------------------------------------------|-------------------|---------|----------------------------------------------------------------------|----------------------------------------|---|----------------------------------------------------------------------|------------------------------|---|----------------------------------------------------------------------|
| <p>XMIMSIM-PyMca Program Location</p> <div> <input type="text"/> <input type="button" value="Browse"/> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |           |                                                                      |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| <p>XMIMSIM-PyMca Configuration</p> <table> <tr> <td>Photon beam polarisation degree:</td> <td>0.99500</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Source horizontal size FWHM (cm):</td> <td>0.00050</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Source vertical size FWHM (cm):</td> <td>0.00010</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Source horizontal divergence (rad):</td> <td>0.00010</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Source vertical divergence (rad):</td> <td>0.00010</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Distance beam source to slits (cm):</td> <td>131.00000</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Distance beam source to sample (cm):</td> <td>100.00000</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Slit width (cm):</td> <td>0.00500</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Slit height (cm):</td> <td>0.00500</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Maximum number of sample interactions:</td> <td>4</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> <tr> <td>Sample layer to be adjusted:</td> <td>0</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> </table> |           |                                                                      |       |            |             |        |                |       | Photon beam polarisation degree: | 0.99500 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Source horizontal size FWHM (cm): | 0.00050 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Source vertical size FWHM (cm): | 0.00010 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Source horizontal divergence (rad): | 0.00010 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Source vertical divergence (rad): | 0.00010 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Distance beam source to slits (cm): | 131.00000 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Distance beam source to sample (cm): | 100.00000 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Slit width (cm): | 0.00500 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Slit height (cm): | 0.00500 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Maximum number of sample interactions: | 4 | <input type="button" value="▲"/><br><input type="button" value="▼"/> | Sample layer to be adjusted: | 0 | <input type="button" value="▲"/><br><input type="button" value="▼"/> |
| Photon beam polarisation degree:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 0.99500   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Source horizontal size FWHM (cm):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 0.00050   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Source vertical size FWHM (cm):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 0.00010   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Source horizontal divergence (rad):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 0.00010   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Source vertical divergence (rad):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 0.00010   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Distance beam source to slits (cm):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 131.00000 | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Distance beam source to sample (cm):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 100.00000 | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Slit width (cm):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | 0.00500   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Slit height (cm):                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 0.00500   | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Maximum number of sample interactions:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 4         | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Sample layer to be adjusted:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | 0         | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| <p>Simulation Control</p> <table> <tr> <td>Number of histories:</td> <td>100000</td> <td><input type="button" value="▲"/><br/><input type="button" value="▼"/></td> </tr> </table>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |           |                                                                      |       |            |             |        |                |       | Number of histories:             | 100000  | <input type="button" value="▲"/><br><input type="button" value="▼"/> |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |
| Number of histories:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | 100000    | <input type="button" value="▲"/><br><input type="button" value="▼"/> |       |            |             |        |                |       |                                  |         |                                                                      |                                   |         |                                                                      |                                 |         |                                                                      |                                     |         |                                                                      |                                   |         |                                                                      |                                     |           |                                                                      |                                      |           |                                                                      |                  |         |                                                                      |                   |         |                                                                      |                                        |   |                                                                      |                              |   |                                                                      |

**Figure S10: XRFMC parameters PyMCA.**

# Experimental – Thresholds values

Table S5 and table Table S6 show the thresholds used to correct the XRF peak areas.

*Table S5: Manually chosen thresholds per elemental transition in counts/s*

| Element transition | Manually chosen threshold [cnt/s] | Element transition | Manually chosen threshold [cnt/s] |
|--------------------|-----------------------------------|--------------------|-----------------------------------|
| AL-K               | 10                                | Br-K               | 50                                |
| Si-K               | 10                                | Rb-K               | 100                               |
| P-K                | 7                                 | Sr-K               | 14                                |
| S-K                | 7                                 | Zr-K               | 30                                |
| Cl-K               | 12                                | Nb-K               | 15                                |
| Ar-K               | 15                                | Mo-K               | 30                                |
| K-K                | 25                                | Cd-K               | 30                                |
| Ca-K               | 11                                | Cd-L               | 15                                |
| Ti-K               | 7                                 | Sn-K               | 50                                |
| Cr-K               | 15                                | Sn-L               | 15                                |
| Mn-K               | 11                                | Sb-K               | 20                                |
| Fe-K               | 6                                 | Ba-K               | 10                                |
| Co-K               | 4                                 | Ba-L               | 10                                |
| Ni-K               | 20                                | W-L                | 200                               |
| Cu-K               | 15                                | Hg-L               | 50                                |
| Zn-K               | 9                                 | Pb-L               | 10                                |
| Ga-K               | 400                               | Pb-M               | 15                                |
| Se-K               | 40                                | Bi-L               | 200                               |

*Table S6: Comments about the manually chosen threshold per elemental transition.*

| Element transition | Comment                                                                                                                         |
|--------------------|---------------------------------------------------------------------------------------------------------------------------------|
| AL-K               | highest value is not conclusive for 10s                                                                                         |
| Si-K               | highest value is not conclusive for 10s                                                                                         |
| P-K                | 7.45 is a peak, 6.19 is not {both at 10s}                                                                                       |
| S-K                | 6 measured 30s is still detectable at 10s its inconclusive, but treshhold should be set at worst case so 10 s. Mind Pb overlap! |
| Cl-K               | highest value is not conclusive for 10s                                                                                         |
| K-K                | Mind Cd overlap! Not much info. 40 is ok, 16 is not.                                                                            |
| Mn-K               | Mind, partly under Ba.                                                                                                          |
| Fe-K               | lowest value still is a clear peak, correct for the 7.85 (from the instrument?)                                                 |
| Ni-K               | shoulder on cobalt                                                                                                              |
| Zn-K               | lowest value still is a clear peak, correct for the 7.85 (from the instrument?)                                                 |

|             |                                                                                |
|-------------|--------------------------------------------------------------------------------|
| <b>Ga-K</b> | overlap with Pb (381.54)/ Zn - dismiss                                         |
| <b>Br-K</b> | overlap Hg                                                                     |
| <b>Rb-K</b> | highest value is not conclusive for 10s<br>(overlap with Pb)                   |
| <b>Zr-K</b> | slight overlap Sr                                                              |
| <b>Cd-L</b> | Area with many low intensity peaks, better<br>use Cd-K or check Cd-L with Cd-K |
| <b>Sn-L</b> | Area with many low intensity peaks, better<br>use Sn-K or check Sn-L with Sn-K |
| <b>W-L</b>  | Overlap with zinc, highest value not<br>conclusive                             |
| <b>Bi-L</b> | Overlap with Pb, don't use                                                     |

# Deconvolution and guidelines for spectra interpretation based on reference paint outs.

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The following figures all refer the section dealing with references.

## Filter & Deconvolution

Figure S11 and Figure S12 present the barium/titanium deconvolution with (Figure S11) and without (Figure S12) the Ti/Al filter. Additionally, Figure S12 supports claims made about the distortion in peak area for zinc and titanium in mixtures.

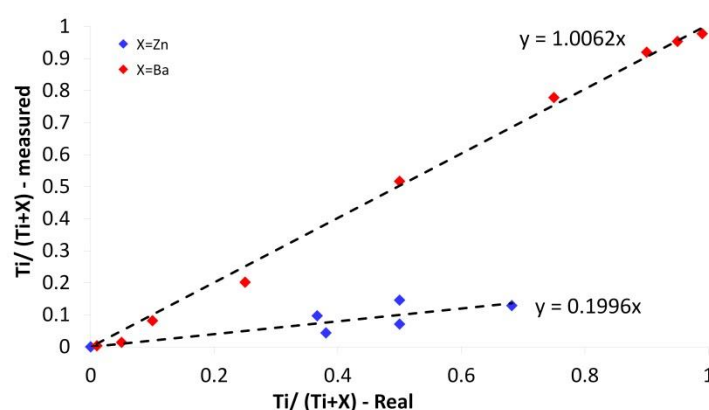


**Figure S11: Peak area ratios of known composition versus measured data for barium-titanium and zinc-titanium. For barium titanium this plot confirms successful deconvolution of the overlapping peaks. For zinc titanium this plots highlights the distortion of real vs. measured values.**

The deconvolution of barium and titanium in spectra measured without filter was reasonably accurate (Figure S12), despite the deconvolution being programmed for measurements using the yellow filter.

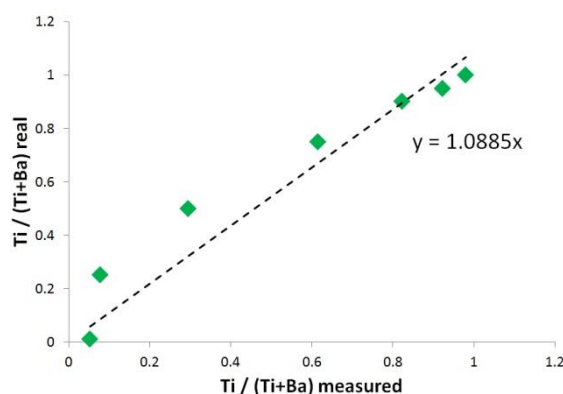


**Figure S12: Titanium Barium deconvolution from data without the yellow filter**

Figure S13 highlights the deconvolution difficulty for overlapping titanium and barium peaks.

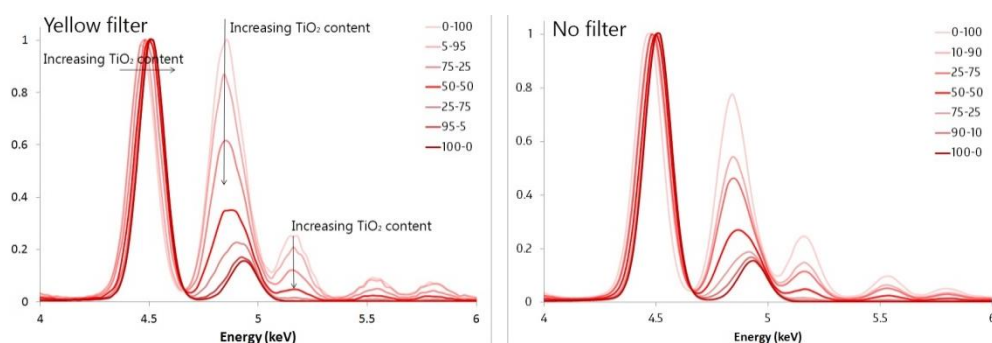


**Figure S13: Spectra of titanium dioxide, barium sulfate mixtures (v/v) with and without the yellow filter.**

## Mixtures & Layers

Additionally the reference paint outs were investigated for guidelines on interpreting spectra of layers and mixtures. The following trends were confirmed/established (based on figures S14-19):

- If sulfur is identified in spectra without lead and in combination with barium and/or strontium this indicates that the barium sulfate is present in the top layer. Any overlaying layer would absorb the signal. Additionally the sulfur is only detected when enough barium sulfate is present: a 0.25 Ba: 0.75 Ti mixture does not show the presence of sulfur.
  - **Guideline I: When sulfur is detected in the absence of lead and presence of barium this indicates that a major amount of barium sulfate is present at the paint surface. The absence of sulfur does not necessarily indicate that barium sulfate is in a lower layer; it can also mean that it is present in low amounts.**
- A thick layer of titanium white absorbs signals any underlying material (confirmed for lead and zinc). A thin layer of titanium white still shows signal from underlying lead or zinc paints).
  - **Guideline II: A measurement of impasto can be considered as a probe of only the top layer.**
- A thin layer of zinc white or lead white is enough to absorb all signal from an underlying titanium white layer.

- **Guideline III: If titanium is detected in combination with zinc or lead it is likely to be present in the top layer (as a mixture with the other element or as thin superimposed layer).**
- When lead white is at the surface there is a known ratio between the Pb-M and Pb-L peak areas. If Pb-M is not detected or the Pb-L/Pb-M ratio is strongly distorted (between 700-800, figure S15) this indicated the lead white is in a lower layer.
  - **Guideline IV: The absence of Pb-M or the distortion of the Pb-L/Pb-M ratio indicates that the lead originates from a lower layer.**

Figure S14 highlight that a thick layers of titanium cancels signal from underlying lead or zinc containing layers. Additionally it shows that a thin layer of lead or zinc cancels out the underlying titanium signal.

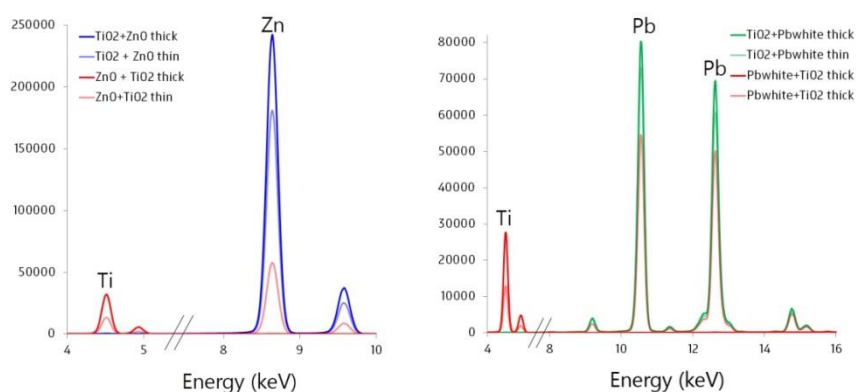


**Figure S14: Spectra of layered structures containing titanium dioxide and [left] zinc oxide or [right] lead white.**

Figure S15 and Figure S16 highlight the claims about lead containing layers in relation to the detection of the Pb-M peak or the Pb-L/Pb-M peak ratio. Supporting spectra can be found in Figure S17 and Figure S18

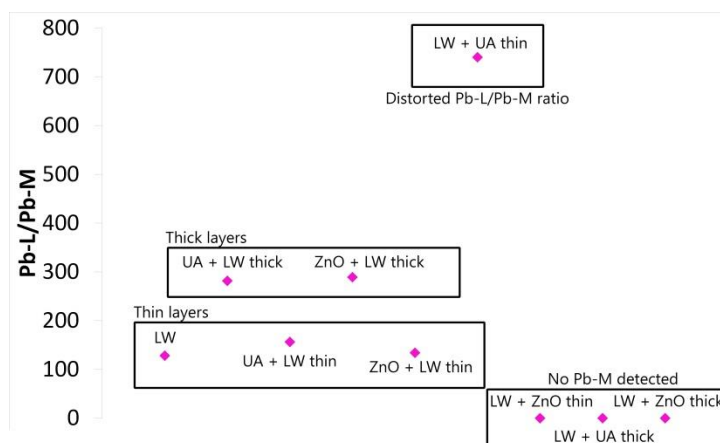


**Figure S15: Pb-L/Pb-M peak area ratios of lead white, zinc white and titanium white layer structures.**

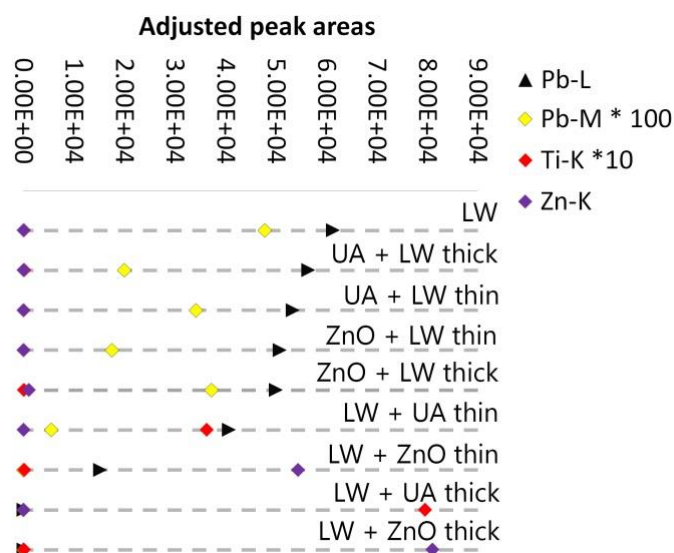


**Figure S16: Overview of peak areas for lead containing layered references . Each line represents one sample and the dots represent the adjusted peak areas. The peak areas are adjusted to fall within the same range so they can be compared. Any data point showing as more than 0 (even adjusted \* 100) can be visually observed in the spectrum.**

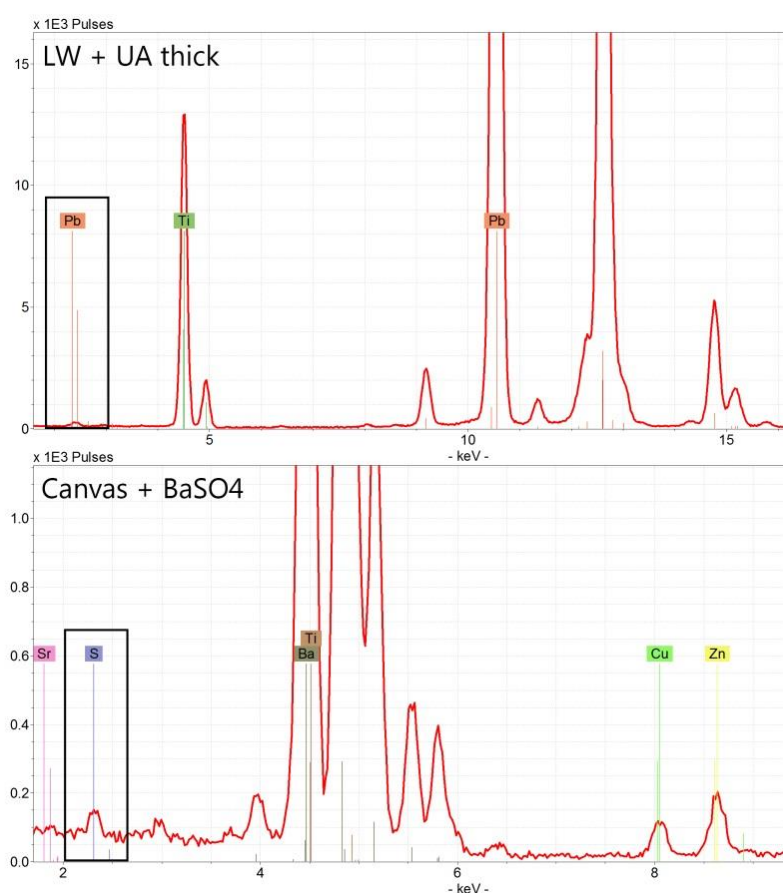


**Figure S17: Visibility of adjusted peak areas in the real spectrum: [top] Pb-M and [bottom] S. No references were measured containing both lead and barium sulfate. In that case deconvolution of these overlying peaks may pose a problem.**

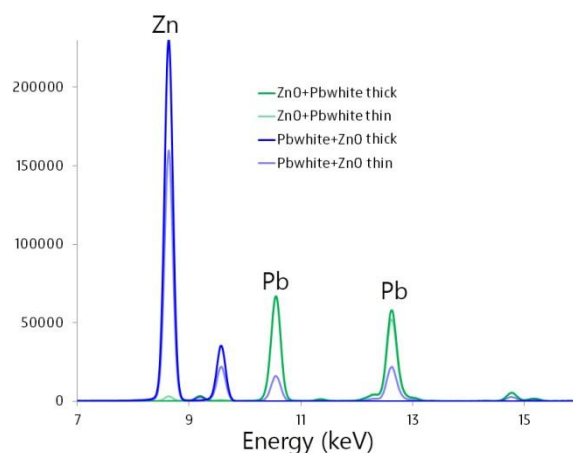


**Figure S18: Spectra of layered structures containing zinc white and lead white.**

Figure S19 indicates adjusted peak areas for several mixtures and layers and Figure S17 provides a supporting spectrum.

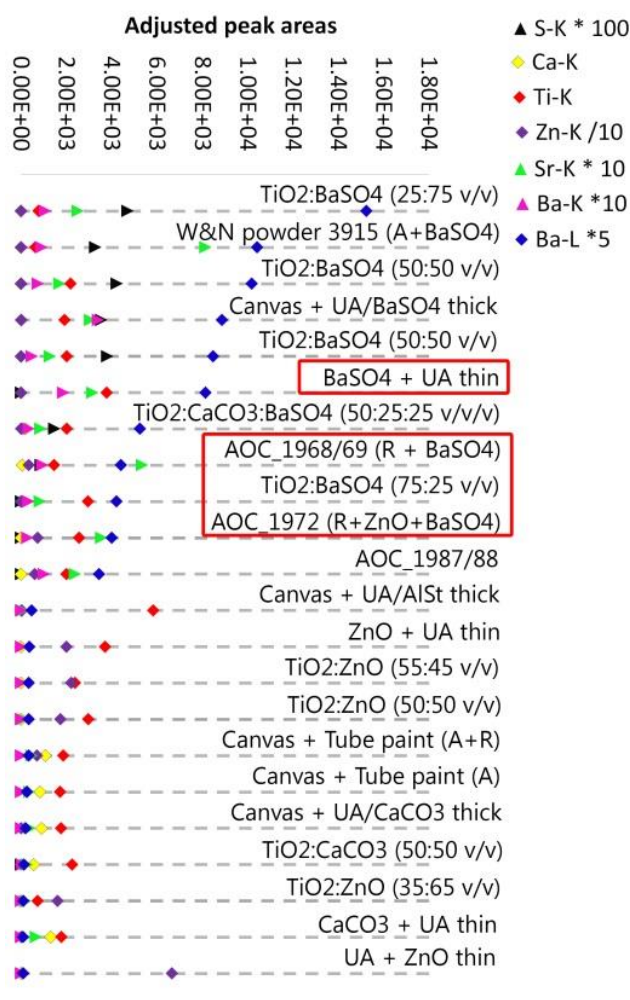


**Figure S19: Overview of peak areas for mixtures and layers. Each line represents one sample and the dots represent the adjusted peak areas. The peak areas are adjusted to fall within the same range so they can be compared. Any data point showing as more than 0 (even adjusted \* 100) can be visually observed in the spectrum.**

# Results & Discussion

Figure S20 and S21 shows the PCA coloring used to cluster figure 4 of the manuscript.

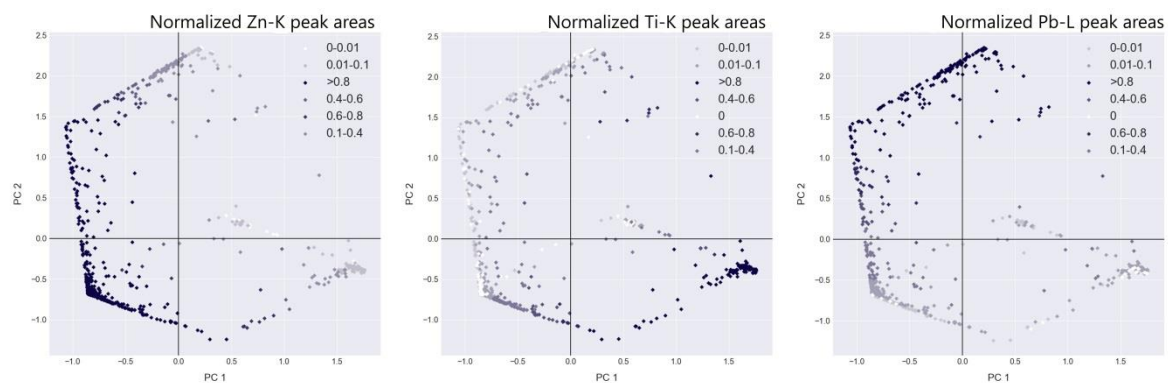


**Figure S20: PCA of all data measured with the yellow filter, corrected for time and threshold normalized to maximum. Colored by main element.**

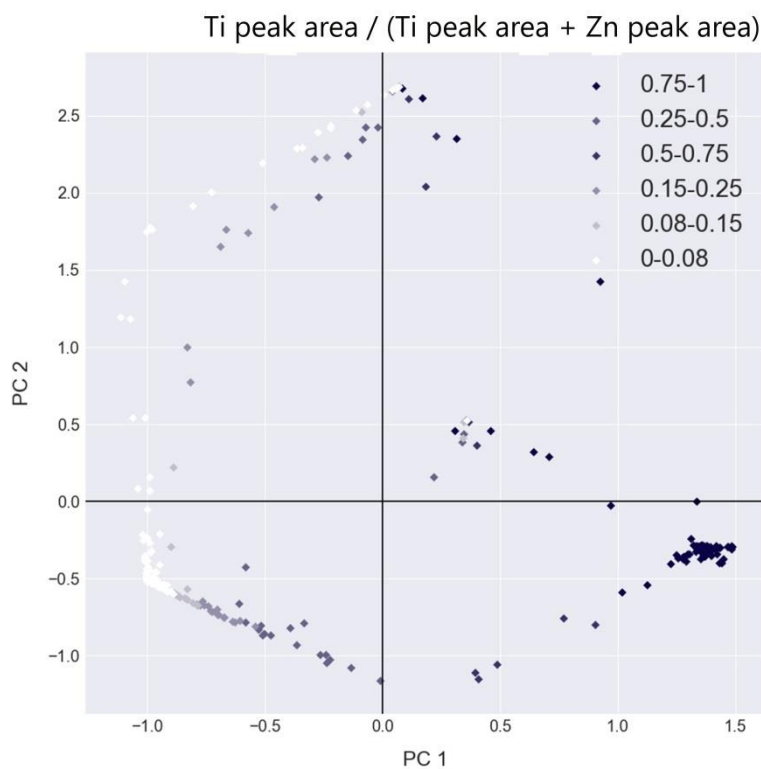


**Figure S21: PCA of all data (time and threshold corrected) from spectra from white areas, averaged per object and normalized to the maximum peak area colored by titanium-zinc ratio.**

Figure S22 show scatterplots indicating anti-correlations in Ti based paints (top) and Zn based paints (bottom).

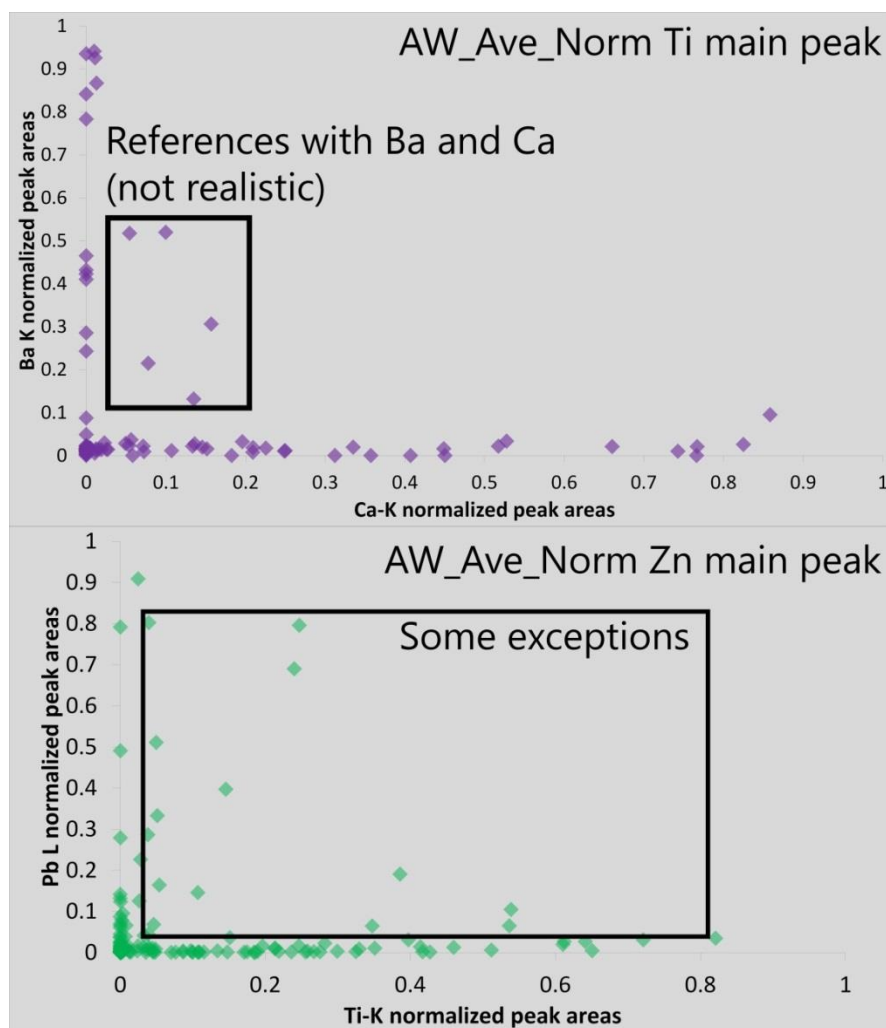


**Figure S22: Scatterplot analysis [top] Barium vs. Calcium and [bottom] lead vs. titanium peak areas for all object where [top] Ti is the main peak and [bottom] Zn is the main peak.**

Figure S23 and Figure S24 show example spectra where the niobium peak (present in UA) is not measured due to the presence of heavier elements. As mentioned in the paper the authors believe that with optimized instrument settings niobium should always be possible to detect.

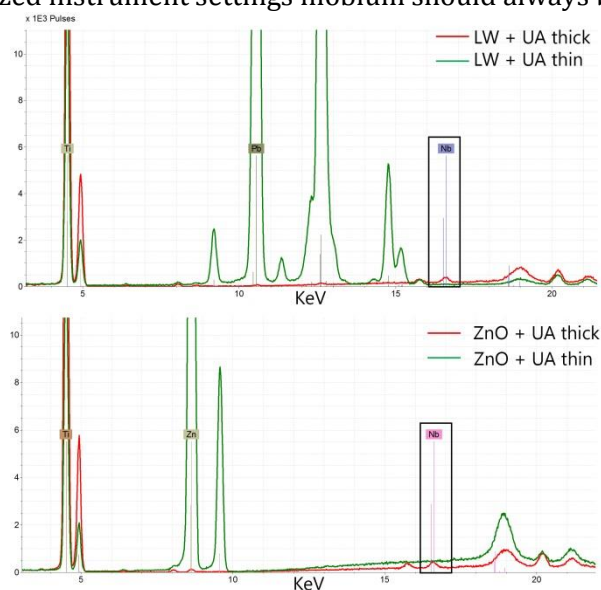


**Figure S23: XRF spectra of reference paints containing [top] lead white (LW) or [bottom] zinc white under a thick or thin layer of uncoated anatase (UA) known to contain Niobium.**

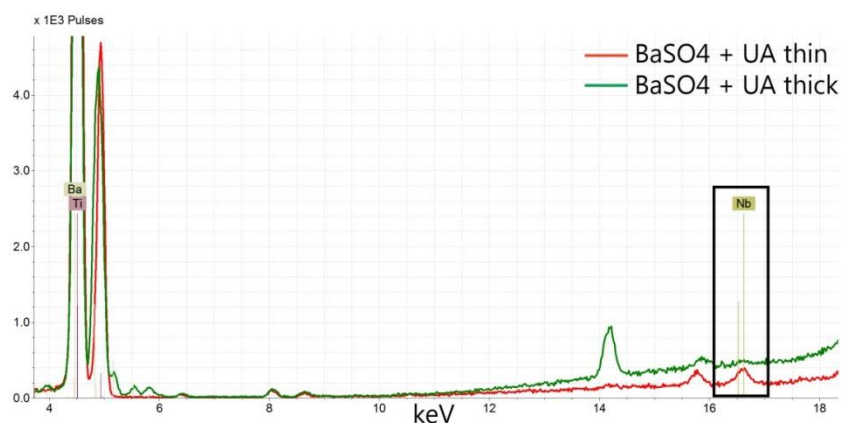


**Figure S24: XRF spectra of reference paints containing barium sulfate under a thick or thin layer of uncoated anatase (UA) known to contain Niobium.**