A micro-invasive technique is presented that enables pigment sampling from individual layers of a painting cross-section by obtaining a furrow 10–50 μm wide of chosen length. Combined with increased sensitivity of lead (Pb) isotope analysis using multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) equipped with a $10^{13}$ Ω resistor or a Pb double-spike technique, the amount of Pb needed for isotopic analysis is drastically reduced, while maintaining a relative 2 SD precision for $^{206}$Pb/$^{204}$Pb of < 0.02%. The methodology proved able to characterize Pb isotope differences within paint layers.

**KEYWORDS:** LEAD WHITE PIGMENT, MICRO-INVASIVE SAMPLING, LEAD ISOTOPES, MC-ICPMS, $10^{13}$ Ω AMPLIFIER

**INTRODUCTION**

Historically, lead white was the most important white pigment used in easel painting until the 19th century, when the more transparent white, zinc oxide, was introduced (Eastaugh et al. 2004). In the early 1920s, a similarly opaque alternative, titanium white, became commercially available. Lead white was synthesized by exposing metallic lead to acetic acid, either by submerging it in vinegar or by the Dutch so-called ‘stack’ process where strips of metallic lead were placed over vinegar in earthenware pots, surrounded by manure which provided heat and CO$_2$ to speed up the process. This would be covered with wooden boards, to
hold the next stack of pots, etc. After several months the lead was covered with the white basic lead carbonate, 2PbCO$_3$·Pb(OH)$_2$. This would be scraped off, washed and dried (Eastaugh et al. 2004).

The interest in the isotopic analysis of lead white stems from the fact that Pb has four isotopes (204Pb, 206Pb, 207Pb and 208Pb), of which only 204Pb is not formed by the radioactive decay of uranium (U) and thorium (Th) (Faure 1986). Pb is found in ore deposits worldwide, and its isotope abundances are a function of the age of the ore deposit and the different geological processes that produce variable U, Th and Pb contents in the ore minerals. Over geological time, different U/Pb and Th/Pb ratios produce different Pb isotope ratios: 232Th decays to form 208Pb, increasing the 208Pb/204Pb ratio, while 235U and 238U decay to form 207Pb and 206Pb, respectively, increasing the 207Pb/204Pb and 206Pb/204Pb ratios while at the same time producing variable 208Pb/206Pb, 207Pb/206Pb and 207Pb/208Pb ratios (Faure 1986). Therefore, different Pb deposits worldwide have different Pb isotope compositions from which it may be possible to reconstruct the provenance of the Pb that makes up pigments or artefacts.

Pb isotope analysis on lead white pigments has been performed since the 1970s in order to determine the provenance of the Pb (Keisch and Callahan 1976). Within Europe, however, some mines have overlapping Pb isotope compositions potentially complicating the interpretation of Pb isotope measurements (Stos-Gale and Gale 2009; Blichert-Toft et al. 2016). This is the case for some British, German and Polish mines. Importantly, however, these mines were generally not in production at the same time. With this knowledge, it may be possible to provide unambiguous attribution for the source of Pb (Gulson 1986). For example, due to different production and trade histories it is possible to distinguish easily between Flemish and Italian lead white because geologically distinct Pb ores were used in the manufacture of lead white north and south of the Alps (e.g., Fortunato et al. 2005; Fabian and Fortunato 2010). Therefore, both the history of lead trade, as well as the active production periods of individual mines, may potentially add relevant information to art-historical research into the attribution of paintings, their geographical provenance and dates (Pollard and Heron 2008). In the field of painting research, however, few extensive studies have been made since the first use of this technique, the most notable being the work of Keisch and Callahan (1976), Fortunato et al. (2005) and Fabian and Fortunato (2010). Pb isotope analysis is being used for painting authentication/attribution purposes (Wallert 2002; Leeuw 2013; Tummers et al. 2019). There are, however, major limitations in such provenance/authentication studies. First, there is no detailed database containing information on the isotopes of lead white in paintings with an authenticated provenance history. Second, a large proportion of existing Pb isotope data from ore samples and pigments was obtained before the introduction of the latest generation multi-collector mass spectrometers and, consequently, may suffer from mass-dependant instrumentation artefacts, which limits the usefulness of some published data.

The third and major issue that hinders such research is the invasive/destructive nature of the technique. Pictorial material for Pb isotope analysis is obtained by manually sampling the painting with a scalpel, a procedure usually performed by trained conservators. Manual sampling, usually as scrapings of lead white areas only, obtains between 10 and 150 μg of material that is subsequently dissolved for chemical purification and isotopic analysis. The destructive nature of sampling has, in the past, limited the number of samples available to build up an extensive Pb isotope database for lead white. Modern mass spectrometry, however, requires only a few to tens of ng of Pb for precise Pb isotope analysis, meaning a few micrograms of paint material are required (Koornneef et al. 2019). This represents much smaller amounts of material than sampled using a scalpel.
Direct sampling from paintings, however, is not the only way to access pictorial material. Many paint samples taken for conservation research already exist as embedded cross-sections containing stratigraphy of paint layer build-ups. The ability to access and study these samples represents a huge opportunity to expand knowledge about Pb-based pigments. Moreover, the study of separate paint layers would allow the heterogeneity of Pb isotopes to be determined within and between different pictorial layers and throughout an individual painting. Sampling from a paint cross-section offers new opportunities and increased access to material. However, to preserve the cross-section, a minimally invasive sampling technique needs to be designed.

This work is part of a collaborative study between the Rijksmuseum and the Vrije Universiteit Amsterdam to address the above issues, and to establish if there are variations in the Pb isotope composition of lead white used in European paintings that could potentially be applied to provenance–authentication purposes. Specifically, it reports a new approach to analysing Pb isotopes in lead white pigment that minimizes the damage to paint cross-sections, providing museums with a quick, precise and minimally destructive method applicable to a broad range of paintings. This goal was achieved by improving the analytical method in two ways. First, the design and manufacture of a method that allows precise sampling of micrograms of pigment from paint cross-sections. Minimally invasive sampling of cross-sections preserves most of the cross-section so that it can be used for further analysis (X-ray fluorescence (XRF), Raman, scanning electron microscope (SEM), transmission electron microscopy (TEM) etc.), allowing conservators and art historians to obtain an holistic analysis of the sample and artwork. Second, developing methods on a multi-collector-inducted couple that uses a Pb double-spike (DS) technique or a $10^{13}$ Ohm resistance amplifier to obtain precise isotopic data on small samples containing $\leq 20$ ng Pb.

Using a mix of $10^{11}$ and $10^{13}$ $\Omega$ resistance amplifiers, where the $10^{13}$ $\Omega$ amplifier is mounted on the cup collecting the $^{204}$Pb beam (the least abundant Pb isotope), allows a drastic reduction in the amount of sample used (Klaver et al. 2015). The use of a high-resistance $10^{13}$ $\Omega$ resistor increases the signal intensity by a factor of 100, while the noise increases by only a factor of 10, improving the signal-to-noise ratio 10-fold according to the Johnson–Nyquist noise equation (Koornneef et al. 2014). In this way, it is possible to reduce the amount of sample by 10 times and still precisely measure the $^{204}$Pb beam. Previous workers have managed to reduce the amount of Pb used for analysis using a combination of different resistor amplifiers. For example, Pb isotope ratios were determined on small glass samples using ultraviolet femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) equipped with a mix of $10^{11}$, $10^{12}$ and $10^{13}$ $\Omega$ resistor amplifiers (Kimura et al. 2015). Pb isotope ratios involving $^{208}$Pb, $^{207}$Pb and $^{206}$Pb were precisely determined, but the accuracy of $^{204}$Pb-based isotope ratios, important in geochemical studies, was poor due to $^{204}$Hg interference.

Isotope analyses on an MC-ICPMS are always subject to large instrumental mass fractionation. Correction of this fractionation is typically performed by analyses of reference materials with known isotopic composition in between analyses of unknown samples (so-called standard sample bracketing—SSB). Using the known isotopic composition of the reference material, an instrumental mass fractionation factor can be calculated and interpolated for sample analyses. This approach, however, can correct neither for short-term fluctuations of the instrumental mass fractionation nor for differences in instrumental mass fractionation between the sample and reference material caused by variations in the sample matrix. The well-established DS technique, which requires at least four stable isotopes on an element, allows for internal correction of the instrumental mass fractionation, making the correction time independent (Dodson 1963). In the case of using a $^{207}$Pb-$^{204}$Pb DS, a sample has to be measured twice: once as a natural sample.
and once with the DS added. This approach further allows for correction for potential mass fractionation that may occur during chemical sample preparation (e.g., Schoenberg et al. 2016). The $^{207}\text{Pb}^{204}\text{Pb}$ DS technique is fully described in the literature (Woodhead et al. 1995; Thirlwall 2000, 2002).

Materials and Methods

Micro-sampling of the cross-section

A precisely controlled sampling tool was developed at Vrije Universiteit of Amsterdam (Fig. 1, a). The concept behind the ‘micro-scalpel’ was to enhance the manual scalpel procedure, substituting the human hand with high-precision controls that can move the tip of a scalpel with micrometre precision. The instrument is designed to allow sampling directly from a paint cross-section. The use of the tool allows control of the amount of material sampled, minimizing the amount of material sampled, thereby reducing material damage and wastage. A sample is obtained by moving the tip of a scalpel across a paint cross-section. The width of the sampling furrow varies by up to 50% dependent on the rheology of the paint. Typically, a sample furrow is between 10 and 50 $\mu$m in width. The depth and length are controlled by the operator (Fig. 1, b).

The result of iterations of a prototype is a portable tool, 20 cm long, 10 cm wide and 10 cm high, which weighs about 2 kg, and can be transported easily to any museum and set up in minutes. Sampling cross-sections in a micro-invasively manner requires around 10 min. The procedure includes cleaning the scalpel to avoid potential cross-contamination. The camera allows the operator to sample exactly, be it a single pictorial layer or single particles of lead white. The micro-scalpel has four degrees of freedom ($x$, $y$, $z$, plus the angle between the cross-section and the scalpel). Owing to its high spatial resolution, the micro-scalpel is operated under a microscope to obtain an optimal view of the sampling site. The sampling procedure consists of placing the cross-section in the cross-section holder (1 in Fig. 1, a). The cross-section layers of interest are then aligned parallel to the scalpel’s tip (6) using the micrometre screw control (2). The scalpel is cleaned between each sampling with alcohol and Milli-Q water. Using the microscope and micrometres (3–5), the tip of the scalpel can be guided into the correct position on the cross-section and a sample taken. The sample is collected with the help of adhesive tape and placed in a 1.5 ml centrifuge tube, previously cleaned with double-distilled 3 M HCl. The adhesive tape introduces a negligible amount of environmental Pb to the sample. After sampling, the cross-section can be re-polished and is then ready for storage or further analysis.

Cross-section mock-up validation

In order to validate the methodology, a paint mock-up was prepared. The micro-scalpel was tested on a cross-section mock-up composed of four layers of white paint on canvas. The micro-scalpel was used to sample each layer of the mock-up separately and analysed for Pb. The layers, starting from the canvas, are: (1) lead white (LWA); (2) titanium white (not analysed), (3) lead white (LW2017); and (4) a final layer of lead–tin–yellow (LTY). The pigments used for layers 1, 2 and 4 were taken from a cabinet in the Rijksmuseum Ateliergebouw. The lead white used to create the third layer was made following the Dutch-stack process starting from commercial lead. The pigments were characterized for Pb isotope composition by conventional sample standard bracketing MC-ICPMS analyses (see below) and are isotopically distinct (Table 1), to
allow any cross-contamination to be assessed. The paint was applied to produce layer thicknesses of around 100–200 μm, to compensate for shrinking during the artificial ageing. Heat-bodied linseed oil was used as a medium for the pigments. After the last layer was applied, the mock-up was aged for 24 h using ultraviolet light.

**Pb purification**

The Pb purification method was modified after Klaver et al. (2015). The samples, placed in a 1.5 mL microcentrifuge tubes, were digested in an ultrasonic bath for 1 h in 1 mL double-distilled 3 M HNO₃. The solution was then transferred to a pre-cleaned 7 mL Teflon beaker. The solution was dried-down on a hotplate overnight. The residue was redissolved in 200 μL twice-distilled 0.7 M HBr and passed through AG⁺⁻ 1-X8 Anion Exchange Resin (analytical grade, 200–400 mesh, chloride form). After eluting the matrix in 0.7 M HBr, the Pb fraction was obtained in 6.5 M HCl, dried down overnight and then nitrated with 50 μL double-distilled 65% HNO₃, and finally dried down and dissolved in 1 ml double-distilled 1% HNO₃. A 50 μL aliquot of this solution was analysed using a X-Series II inductively coupled plasma mass spectrometer (ICPMS) (Thermo Scientific) to determine the Pb content. Once the Pb content is known, a 1.7 mL 50 ppb solution of Pb in 1% HNO₃ is prepared for analysis. Total procedure blanks were prepared following the same procedure and spiked with a 208Pb spiked solution with known isotopic composition to determine the amount of Pb in the blank using the isotope dilution method. The analytical-blank varied between 5 and 50 pg Pb.

**Pb isotope analysis by MC-ICPMS**

*Standard sample bracketing* Large Pb samples (> 80 ng) are routinely analysed at the VU of Amsterdam by standard sample bracketing (SSB) on a 50 ppb solution of Pb using a Thermo
Table 1  Results of the analyses of the three lead (Pb)-based pigments. The pigments were analysed as raw material and after application as paint on canvas (‘sampled’)

<table>
<thead>
<tr>
<th>Pb (ng)</th>
<th>$^{206}$Pb/$^{204}$Pb 2 SD</th>
<th>$^{207}$Pb/$^{204}$Pb 2 SD</th>
<th>$^{208}$Pb/$^{204}$Pb 2 SD</th>
<th>$^{207}$Pb/$^{206}$Pb 2 SD</th>
<th>$^{208}$Pb/$^{206}$Pb 2 SD</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTY raw</td>
<td>SSB 80</td>
<td>18.6692</td>
<td>0.001</td>
<td>15.6897</td>
<td>0.0009</td>
<td>38.1146</td>
</tr>
<tr>
<td>LTY sampled</td>
<td>SSB 80</td>
<td>18.6743</td>
<td>0.0056</td>
<td>15.6937</td>
<td>0.003</td>
<td>38.1242</td>
</tr>
<tr>
<td>SSB 10$^{13}$</td>
<td>30</td>
<td>18.6661</td>
<td>0.0031</td>
<td>15.6864</td>
<td>0.0026</td>
<td>38.1048</td>
</tr>
<tr>
<td>SSB 10$^{13}$</td>
<td>15</td>
<td>18.6673</td>
<td>0.0063</td>
<td>15.6885</td>
<td>0.0051</td>
<td>38.1111</td>
</tr>
<tr>
<td>LW2017 raw</td>
<td>SSB 80</td>
<td>17.9072</td>
<td>0.0014</td>
<td>15.6043</td>
<td>0.0012</td>
<td>37.954</td>
</tr>
<tr>
<td>LW2017 sampled</td>
<td>SSB 80</td>
<td>17.9957</td>
<td>0.0009</td>
<td>15.6029</td>
<td>0.0018</td>
<td>37.9496</td>
</tr>
<tr>
<td>SSB 10$^{13}$</td>
<td>30</td>
<td>17.9983</td>
<td>0.0054</td>
<td>15.6048</td>
<td>0.0034</td>
<td>37.9535</td>
</tr>
<tr>
<td>SSB 10$^{13}$</td>
<td>15</td>
<td>17.9973</td>
<td>0.0099</td>
<td>15.6046</td>
<td>0.0083</td>
<td>37.9538</td>
</tr>
<tr>
<td>DS</td>
<td>60</td>
<td>17.9922</td>
<td>0.0122</td>
<td>15.6003</td>
<td>0.0108</td>
<td>37.9433</td>
</tr>
<tr>
<td>LWA raw</td>
<td>SSB 80</td>
<td>16.4476</td>
<td>0.0016</td>
<td>15.4893</td>
<td>0.0015</td>
<td>36.2342</td>
</tr>
<tr>
<td>LWA sampled</td>
<td>SSB 80</td>
<td>16.4481</td>
<td>0.0023</td>
<td>15.4884</td>
<td>0.0012</td>
<td>36.2293</td>
</tr>
<tr>
<td>SSB 10$^{13}$</td>
<td>30</td>
<td>16.4527</td>
<td>0.0023</td>
<td>15.4928</td>
<td>0.0025</td>
<td>36.2407</td>
</tr>
<tr>
<td>SSB 10$^{13}$</td>
<td>15</td>
<td>16.4509</td>
<td>0.0039</td>
<td>15.4911</td>
<td>0.0034</td>
<td>36.2359</td>
</tr>
<tr>
<td>DS</td>
<td>60</td>
<td>16.4455</td>
<td>0.0007</td>
<td>15.486</td>
<td>0.0004</td>
<td>36.2238</td>
</tr>
</tbody>
</table>

DS, double-spike; LTY, lead–tin–yellow; LWA, lead white; SSB, standard sample bracketing.
Scientific Neptune MC-ICPMS. This method requires around 80 ng Pb in order to have a 1.7 mL solution. Measurements were performed using a desolvating nebulizer system CETAC Aridus II operating at approximately 4–5 L min\(^{-1}\) of Ar sweep gas, 0.01–0.02 L min\(^{-1}\) nitrogen and temperature settings of 110°C for the spray chamber and 160°C for the membrane. The room is kept at a constant 20 ± 1°C. After the instrument was tuned, it was allowed to stabilize for 2–3 h. Pb signals were usually about 0.2 V ppm\(^{-1}\) on Faraday cups equipped with a 10\(^{11}\)Ω amplifier. A gain calibration was performed on the 10\(^{11}\)Ω amplifiers once per week. An analysis consisted of one block of 100 cycles of 4 s integration time. Instrument operating parameters were: RF power: 1290 W; mass assignment to Faraday cup detectors: \(^{201}\)Hg L4, \(^{202}\)Hg L3, \(^{204}\)Pb L2, \(^{205}\)Tl L1, \(^{206}\)Pb C, \(^{207}\)Pb H1, \(^{208}\)Pb H2, \(^{209}\)Bi H3.

The long-term precision, expressed as 2 standard deviations (SD) over two years, was 0.0031 for \(^{206}\)Pb/\(^{204}\)Pb, 0.0034 for \(^{207}\)Pb/\(^{204}\)Pb and 0.00114 for \(^{208}\)Pb/\(^{204}\)Pb.

\(10^{13}\)Ω resistor

The use of \(10^{13}\)Ω amplifiers reduces drastically the amount of sample needed for analyses without affecting the precision and accuracy of the measurement. Here the SSB method is used with a \(10^{13}\)Ω resistor amplifier connected to the Faraday cup, which collects the \(^{204}\)Pb beam, while all the other Faraday cups were connected to \(10^{11}\)Ω amplifiers. This set-up reduces the noise on the small \(^{204}\)Pb ion beam, improving the precision on any Pb isotope ratio involving \(^{204}\)Pb (Klaver et al. 2015). Data acquisition consisted of one block of 100 cycles of 4 s integration with an uptake of 150 μL min\(^{-1}\), consuming around 1.5 mL of solution. As the \(10^{13}\)Ω amplifier has a slower response time than the \(10^{11}\)Ω amplifier, a Tau factor was used to correct for this difference (Kimura et al. 2015). This method was tested by running multiple analyses of 5, 10 and 20 ppb Pb solutions of NBS981, corresponding to a sample amount of 7.5, 15 and 30 ng Pb, respectively. The long-term precision was monitored over several months (July–November 2019).

Double-spike (DS) method

Details of the \(^{207}\)Pb–\(^{204}\)Pb DS composition have been published previously (Klaver et al. 2015). Using this DS requires separate analyses of a natural and a DS mixed solution. This was achieved by dividing the sample into two aliquots and spiking one 1:1 with the \(^{207}\)Pb–\(^{204}\)Pb DS. The DS was added to three different natural Pb (Pbnat) concentrations of NBS981: 5, 10 and 20 ppb. A sample analysis comprised three blocks of 30 cycles of 4 s integration and required 1.5 mL of solution with an uptake of about 150 μL min\(^{-1}\). Because a sample must be analysed twice in the DS method, the amount of Pb needed for the analysis of the three different concentrations was 15, 30 and 60 ng, respectively. In this study, only \(10^{11}\)Ω amplifiers were used in combination with the DS technique. Raw data were reduced using the iterative solution reported by Compston and Oversby (1969), with the only difference being that the linear fractionation law is replaced by the exponential law. In order to have an estimation of the long-term precision of the DS method, the reference material NBS981 was analysed over several months (July–November 2019).

RESULTS

The Pb isotope results of three of the pigments used for the mock-up are reported in Table 1 and shown in Figure 2. The pigments were analysed as raw material (80 ng Pb in SSB mode with
10^{11} \Omega \text{ amplifiers}) and after sampling with the micro-scalpel. The material sampled with the micro-scalpel was analysed using different analytical methods. The results demonstrate that the isotopic ratios for the individual pigments analysed as raw material and from the cross-section obtained with the micro-scalpel are indistinguishable within uncertainty (Fig. 2, a–c). Thus, it was possible to sample a single layer of paint without contamination from the adjacent layers (Fig. 2, d).

The reference material NBS981 was analysed multiple times in three different concentrations, corresponding to sample amounts of 7.5, 15 and 30 ng Pb, respectively, using both amplifier configurations as described above and the SSB correction method (Table 2 and Fig. 3, a). All data are accurate within uncertainty (Thirlwall 2002). In general, the long-term precision (2 SD) improves with increasing Pb concentration, and using a 10^{13} \Omega \text{ amplifier for the } ^{204}\text{Pb beam improves the long-term precision compared with the standard } 10^{11} \Omega \text{ amplifier configuration (Fig. 3, c). In particular, analyses of 7.5 ng Pb (corresponding to a 5 ppb solution) with the } 10^{13} \Omega \text{ amplifier resulted in a 2 SD precision which is comparable with that of a 50 ppb Pb solution using only } 10^{11} \Omega \text{ amplifiers (Table 3 and Fig. 3, c).}

The DS technique (Table 2 and in Fig. 3, b) was tested with } 10^{11} \Omega \text{ amplifiers only. Again, the data obtained for NBS981 were accurate within uncertainty (Thirlwall 2002). The long-term precision improves with increasing Pb concentration, but is in general poorer than for the SSB technique (with and without } 10^{13} \Omega \text{ amplifier) with Pb_{nat} concentrations < 20 ppb (Fig. 3, c).

DISCUSSION

Micro-scalpel sampling

The micro-scalpel method proved to be precise, easy to use and fast in sampling cross-sections. Despite ageing, the mock-up, however, likely has different mechanical properties compared with historical paintings. Sampling several historical cross-sections has shown that different layers in a painting have different physical properties and care is required to obtain optimal sample sizes. Paint layers of ancient paintings are generally more rigid and brittle than the mock-up, but were found to record a large range in rigidity. This can lead to differences in the quantity of material obtained during sampling. Figure 1 (b) shows an SEM image of a sampled cross-section from a historical painting. The blue area represents a desired sampling volume, whereas the red area shows that a large particle was removed from one part of the furrow. However, even suboptimal sampling with the micro-scalpel, resulting in relatively large furrows, provides samples that are considerably smaller than samples obtained by manual sampling.

DS technique

The DS method proved to be an efficient way to improve the measurement precision, however, only for relatively large sample sizes (> 60 ng). Despite using less sample material (60 ng for the two analyses on a 20 ppb Pb_{nat} solution) the 2 SD of } ^{206}\text{Pb}/^{204}\text{Pb is comparable or better than the 2 SD obtained by the SSB method using 80 ng (50 ppb Pb_{nat} solution) (Table 3). In particular, the precision of the } ^{208}\text{Pb}/^{204}\text{Pb ratio improved by a factor of 2. For lower Pb amounts, however, the precision of this technique is relatively poor. That is, for 15 ng Pb, the long-term precision is about four times worse compared with analyses of the same amount of Pb by SSB using the } 10^{11} \Omega \text{ amplifiers only. Here the signal intensity of the } ^{204}\text{Pb beam in the natural run is the limiting factor. Typical } ^{204}\text{Pb signals were about 40 mV for a 5 ppb Pb_{nat}, resulting in a relatively low
The long-term 2 SD precision is used as criterion for deciding which method is best suited for which range of sample size (Table 3 and Fig. 3, c). Based on these data, and taking into account the potential effect of the analytical blank and the quantity of material required for analysis, it is
<table>
<thead>
<tr>
<th>Replicates</th>
<th>Pb (ppb)</th>
<th>Pb (ng)</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$ 2 SD</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$ 2 SD</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$ 2 SD</th>
<th>$^{207}\text{Pb}/^{206}\text{Pb}$ 2 SD</th>
<th>$^{208}\text{Pb}/^{206}\text{Pb}$ 2 SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS long-term reproducibility</td>
<td>14</td>
<td>5</td>
<td>15</td>
<td>16.9356</td>
<td>0.0171</td>
<td>15.4927</td>
<td>0.0145</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>10</td>
<td>30</td>
<td>16.9414</td>
<td>0.0054</td>
<td>15.4989</td>
<td>0.0048</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>20</td>
<td>60</td>
<td>16.9412</td>
<td>0.0029</td>
<td>15.499</td>
<td>0.0026</td>
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<tr>
<td>Mix of 1011 and 1013 resistor long-term reproducibility</td>
<td>16</td>
<td>5</td>
<td>7.5</td>
<td>16.9418</td>
<td>0.0036</td>
<td>15.4992</td>
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<td></td>
<td>16</td>
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<td>16.9425</td>
<td>0.0032</td>
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<td></td>
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<td>16.9414</td>
<td>0.0028</td>
<td>15.4993</td>
<td>0.0025</td>
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</table>
Figure 3  Measured $^{206}$Pb/$^{204}$Pb ratios of different amounts of reference material NBS981. (a) Analyses corrected with the double-spike (DS) method compared with the true value of the NBS981 (Thirlwall 2002). For each sample size of Pb analysed, the mean is indicated by a solid horizontal line; the 2 SD precision of the replicates is represented by the blue shaded area. Internal 2 SE errors are smaller than the symbol size. (b) Analyses with the $10^{13}$ Ω resistor amplifier on $^{204}$Pb. The true value of the NBS981 (Thirlwall 2002) is shown for comparison. The mean and 2 SD of replicates is as shown in (a). Internal 2 SE error bars are not shown (for the data and discussion, see the additional supporting information). (c) Comparison between the long-term precision of the different methods. The long-term precision is reported as two times the relative deviation standard (2RSD) against the amount of Pb analysed (ng). [Colour figure can be viewed at wileyonlinelibrary.com]
possible to conclude which method is most appropriate. When sample size is not a limitation (i.e., > 80 ng Pb), the SSB method using standard 10\textsuperscript{11} Ω amplifiers provides excellent precision, with a long-term 2 SD for the 206Pb\textsuperscript{204}Pb and 207Pb\textsuperscript{204}Pb ratios of 0.0031 and 0.0034, respectively. Thus, two samples having values of 206Pb\textsuperscript{204}Pb and 207Pb\textsuperscript{204}Pb with a difference > 4 SD of the long-term reproducibility, 0.0062 and 0.0068, respectively, are analytically different and can be resolved. The DS methods allows a reduction in the amount of sample to around 60 ng (20 ppb Pbnat solution), while yielding a better precision (Fig. 3, c). The method, however, requires two runs per sample and the use of a DS solution, resulting in longer and more expensive analyses. Use of a DS is especially advisable for the analysis of Pb samples that cannot be completely separated from their matrix, which can alter the instrumental mass fractionation relative to the reference material and thus cannot completely be corrected with the SSB method.

The SSB method using the 10\textsuperscript{13} Ω amplifier reduces the required amount of sample drastically (up to 10 times), while maintaining a 2 SD precision comparable with an SSB corrected analyses of large samples (i.e., 80 ng) using 10\textsuperscript{11} Ω amplifiers. As this precision is sufficient to resolve the large isotopic differences recorded by Pb white pigments (Fabian and Fortunato 2010) and thus to provenance individual pigments, the 10\textsuperscript{13} Ω technique offers the possibility to reduce the amount of sample by a factor of 10.

**CONCLUSIONS**

The aim of developing a fast, accurate, precise, micro-invasive and micro-destructive method in order to sample and analyse painting material, while reducing the amount of sample needed for the analysis, has been achieved. The sampling procedure, using the ‘micro-scalpel’, gives the operator the possibility to sample directly from cross-sections, allowing the sampling of single layers. It is also possible to sample specific areas and/or particles of pigment. The collected sample retains the isotopic composition of the pictorial layer, allowing the characterization of different lead white layers within a painting. In this way, it is possible to assess the heterogeneity of
lead white within a painting. Importantly, sampled cross-sections can be re-polished and reused for other investigations.

Different analytical methods were successfully developed that require only micrograms of paint samples to assess the isotopic values of lead white. In particular, the use of the SSB method with a $10^{13}$ Ω resistor amplifier has been tested and shows promising results on the analyses of small samples. The long-term precision of this method on a sample containing 7.5 ng Pb is comparable with the SSB method with standard $10^{11}$ Ω resistor amplifiers on 80 ng Pb. This means that the amount of sample has been reduced by a factor 10. The usage of a DS method allows a reduction of the amount of sample needed by approximately 40%, while retaining the same accuracy and improving the precision of the measurement. This method is especially suitable for samples with residual matrices after chemical separation of Pb, when high blank contributions due to repeated chemical purification are to be avoided. Further work is required in order to optimize a method that combines the DS technique with the use of $10^{13}$ Ω resistor amplifiers.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**Data S1. Supporting Information**

Figure S1 Measured relative standard error (RSE) of different lead (Pb) isotope ratios relative to $^{204}$Pb beam intensity ($10^{11}$ Ω scale). Data were measured with $10^{11}$ Ω amplifiers following theoretical predictions based on counting statistics and Johnson–Nyquist noise (solid lines) for $^{206}$Pb/$^{204}$Pb (blue), $^{207}$Pb/$^{206}$Pb (grey) and $^{208}$Pb/$^{206}$Pb (black). Data were measured with a $10^{13}$ Ω amplifier on $^{204}$Pb and are about five times larger than predicted.