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Detecting art forgeries using LA-ICP-MS incorporating the in situ application of laser-based collection technology

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Abstract

The nature of art lends itself to forgery as a skilled and determined forger can mimic the techniques and styles of an artist to a level where even an expert can be duped. The authentication of paintings is a subjective process, but modern techniques may provide the means to provenance artist pigments based on elemental composition. This study applies laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to the analysis of artist paints from different manufacturers to identify variation between the elemental association patterns of these materials. The technique facilitates comparison of the paints used by an artist with produced works of art to assist provenancing initiatives of questioned materials. The effects of the trace element profiles of the backing substrate and binder on analytical data were also identified. By applying the technique to paint scraped from real paintings, a limited database was created to allow comparison to be made with some of Australian artist, Kathleen O'Connor's artworks and assist in determining production chronology. Data from this study were able to facilitate comparison of blue paints from two different paintings and confirm their co-provenance consequently determining the relative production date of a separate painting of previously unknown age.

Preliminary trials of a prototype collection device designed to reduce damage and allow for in situ sampling of artworks were also undertaken. The device, which allows direct laser-based sampling of a complete painting, was tested using a Francis Ryan painting. The prototype allows for the collection of debris directly generated by LA-ICP-MS of a predefined area of a painting prior to subsequent analysis using direct LA-ICP-MS. This collection method significantly minimizes the amount of damage produced by conventional sampling methods. Analyses of the debris collected, using the prototype, were found to be comparable to the scrapings of equivalent paint analysed using direct LA-ICP-MS analysis.

Keywords: Forgery; Artist paints; Provenancing paintings; LA-ICP-MS

1. Introduction

Art forgery has existed as long as there have been valuable and admired works of art to forge. By studying the techniques and styles of an artist, a skilled, determined forger can produce a copy that is extremely difficult to distinguish from an original. To make matters worse, the authentication of artwork is a subjective process relying heavily on the knowledge and experience of the art expert charged with the task. In addition, as technology and knowledge increases, and becomes more available to the criminal fraternity, the ability to differentiate between the original authentic work and a forgery becomes increasingly difficult. The forgery of modern art may often provide fewer challenges than the forgery of older material as the copy media have a much greater chance of being equivalent, easily available and the problems associated with ageing modern equivalents to appear old become insignificant. Due to these increasing difficulties, a new, reliable method of art authentication that does not rely upon the interpretation of styles or technique is required. The use of trace element distribution patterns (fingerprints) of the paint pigments represents one such possible technique.

Natural and synthetic pigments are subject to various geological, mining and manufacturing processes, which are unique to each manufacturer and will lead to batch and inter-

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manufacturer differences. In order to use this concept to provenance paintings, it is not merely necessary to analyse the paint itself. The effect of the elemental composition of the binder and the support matrix on which the paint is applied need to be determined and their relative contribution to the pigment trace element pattern established before an accurate elemental fingerprint of the pigment can be determined.

There are four main constituents in an artists' paint: the pigment, binder, diluent and additives. Additives are generally present at low concentration but provide important properties such as colourfastness to the paint. The diluent provides a viscous medium by which the pigment and binder may be spread onto the surface. Binders may have many forms including acrylic resin or oil but all function as an adhesive between the pigment and intended surface. The pigment provides the colour to the paint [1].

Pigments can essentially be classified as either inorganic or organic [2]. While most modern organic pigments are synthetic, there are still some that are derived from plant dyes. Inorganic pigments may be sourced from natural ores [3]. However, due to health and environmental reasons, these are being phased out in preference to synthetically produced varieties. The manufacturing process varies within the industry with the actual process a trade secret, which accentuates differences between brands.

Understanding the manufacturing process of common pigments allows the forensic scientist to understand how trace elements may become incorporated into the final product, and the validity of the concept of using their association pattern in the paint as a provenance establishment technique. For example, titanium dioxide (TiO_2) is the most common of the white pigments as it has a high hiding power (ability to conceal the supporting substrate) [4]. However, in oil the TiO_2 dries as a spongy film, which is unsuitable for artistic purposes, and hence other pigments such as inert barium sulfate or zinc oxide are blended for support. The TiO_2 is refined from the three forms of ilmenite ore (rutile, brookite and anatase). Rutile is refined by the "Tetrachloride Process" which produces titanium tetrachloride. Subsequent oxidation yields solid TiO_2. Anatase and brookite are refined by the addition of sulfuric acid to ilmenite, which allows for the separation of the ferrous sulfate and the isolated titanium sulfate solution is hydrolysed, purified and calcined [5].

The brown raw umber is a natural pigment of iron oxide with magnesium oxide. The raw ore is obtained from Cyprus and is generally washed, slurried, dried and milled. The hue depends on the calcination period, temperature and raw materials used [4]. Cadmium yellow is based on the naturally occurring cadmium sulphides, generally found as an impurity in zinc ores or in lesser quantities as the mineral Greenockite [6]. The size of the pigment particles affects the shade of the paint, with smaller particles resulting in a paler shade. Yellow light is produced by the co-precipitation of Zn with the cadmium sulphide [6]. Alizarin red (or 1,2-dihydroxyanthraquinone) is a synthetically produced organic pigment [7]. Vermillion red was traditionally based on mercury(II) sulphide, but due to its toxicity, the pigment is now synthetically produced as monoazo red or cadmium selenosulphide with arylamide yellow [8].

Of the media available to the artist, oils, acrylics and water are by far the most common. When painting with oil, the pigment is suspended throughout an oil binder and diluted with an organic diluent, an example being linseed oil diluted with spirits of gum turpentine. The organic diluent evaporates as the paint dries, a process taking anywhere from 24 h to several years. Acrylic paints have an acrylic polymer emulsion as the binder. This synthetic polymer was developed in the 1930s, but only commercially produced in the 1950s. Acrylic paints are popular due to the ease with which they mimic other media simply by varying the diluent concentration, which is water [10]. Watercolour paints consist of pigments that are very finely ground and distributed through an aqueous solution of gum, which is then diluted enormously with water [9].

The support substrate refers to the surface on which the paint is applied. The three supports that are discussed in this report are watercolour paper, canvas and Masonite. Masonite is a tough commercial wallboard that is available in a wide range of sizes. This has lead to its increasing popularity as a support for many artists. Watercolour paper is specifically designed for the use of watercolour paints and is predominantly a cellulose-based material. Canvas is the oldest and the most frequently employed support of the three. It is generally woven from cotton or linen or less commonly hemp. Before use the canvas is usually stretched out and fixed with a primer that renders the support less absorptive.

Previous methods for the identification of forgeries have dealt with identifying the composition of the pigments present and relating it to pigments available at the supposed time of production of artwork, such as the introduction of cadmium yellow litopone (cadmium sulfide with $BaSO_4$) in 1927 or Cerulean blue (cobalt stannate) in 1850 [10]. However, the present method works by finding inconsistencies in the trace element patterns of specific pigments in the palette used by a specific artist and thereby indicating the impossibility of the pigment being used by that artist, rather than positively identifying a painting as, for example, attributable to Van Gogh or Picasso on the basis of the availability of a specific pigment used in a painting at the time of manufacture of the painting.

McCrone [11] in his article titled 'Artful Dodgers', mentions a number of instrumental methods currently adopted to identify forgeries. These include ultraviolet and polarised light microscopy, radiocarbon dating, X-rays (including XRD and XRF), which can reveal information regarding the date of the artwork, layers of hidden paint and areas that have been restored. Infrared spectroscopy is also a commonly employed method, but is most applicable to the detection of organic compounds. One particular method McCrone employed himself, in the identification of a painting by Edouard Manet, was electron probe X-ray microanalysis. This technique provided a quantitative measure of the elements that were present and was one of the few references that described looking at the elements specifically.

This paper details an investigation of a range of commercially available artists' paints to identify differences in elemental concentrations between brands, manufacturers, countries, binders and substrates. The analysis of the trace elements present was undertaken using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). This technique facilitates the analysis of solid material by ablation of tiny craters (approximately 20–50 μm in diameter). The material contained within these craters is volatilized into an argon plasma where it is ionized and passed into a mass spectrometer. Here the concentrations of up to 60 elements, at levels below one part per billion, are undertaken. The analytical procedure takes approximately 2 min and results in inconsequential "damage" to the artwork itself. One problem with this technique is that it is confined to relatively small samples, approximately 50 mm × 50 mm. This is obviously of limited applicability to artworks unless a sample is scraped from the canvas for subsequent analysis. While this has been the practice on the past, it is obviously unsatisfactory and can result in observable visual damage. Consequently, significant research has been undertaken to develop a methodology whereby the entire painting could be mounted for analysis and only the extremely small laser pits used as sampling sites. In this way, "damage" to the painting is reduced to an area unobservable to the naked eye and additionally spatial refinement ensures that cross contamination from adjacent and mixed colour areas of the painting will not occur thereby increasing the robustness of the fingerprint and its acceptability as definitive evidence.

In all the previously described analyses, samples have to be removed from the painting using a scalpel, risking damage to the artwork and contamination of the paint flake. Therefore, a method of sampling the painting without the need to cut out flakes has been required for some time. The device proposed in this paper will allow for the sampling and direct analysis of samples of paint in a painting of interest with minimal damage to the painting itself. The device compromises a specifically designed cell, which is positioned over the surface of the painting and allows for the direct ablation of the painting area of interest. The debris created by the laser is then transported using an argon carrier gas and collected on an in-line membrane filter. This filter is then transported to the laboratory for standard laser ablation ICP-MS analysis. This device when completed will provide a means of sampling paintings without the need to provide scrapings for analysis and can be used without the need to remove the artwork from a collection or museum storage facility.

Using both direct LA-ICP-MS of pigments and this technique, it has been possible to establish trace element spectral patterns (fingerprints) for oil, watercolour and acrylic pigments and to identify specific manufacturers. In addition, the examination of historical material, to potentially trace the changes in pigments used by a specific artist (Kathleen O'Connor) from 1911 to 1962 was also undertaken.

2. Experimental

2.1. Instrumentation

A Thermo Analytical PQlll TurboPlus inductively coupled plasma mass spectrometer incorporating a Fisons High Resolution Nd-YAG 266 nm laser accessory was used to acquire the element profile of all samples investigated.

A VG Elemental Nd-YAG laser operating in Q-switched mode at the fundamental wavelength of 1064 nm was used to ablate the paintings in the prototype. The laser has been altered to hold the quartz prototype ablation and collection cell. The door has been lengthened, a new manual stage movement and cell holder custom designed and manufactured specifically for the purpose sampling objects larger than the standard ablation cell. The debris created by the laser is transported using the positive pressure of argon, in an outer sheathing cell, to carry the debris through an inner cell and onto an in-line membrane filter. An oil-less vacuum pump is attached to the outlet of the cell by a length of plastic tubing to assist with the clearing of the cell after each ablation and the changing of filters from the holder. Argon is introduced into the outer sheath cell and regulated using a Fisher and Porter flow meter to a flow of 0.5 L min^{-1}.

The cell is cleaned using Aqua Regia at each change in sample type and the filter holder and interface tubing are also changed with each sample type. The tubing is also changed with each sample type change.

2.2. Samples

2.2.1. Pigments

The elemental composition of paints representing four basic colours, cadmium yellow (light and medium), white (titanium and zinc), red (alizarin and vermilion) and brown (raw umber), were investigated. In total, forty four paint samples were selected from six brands of Artist's paint produced by five different manufacturers. The details of the colour, media and manufacturer of each sample are listed in Table 1. Each sample was placed on a Perspex disc and mixed with a small quantity of cyanoacrylate glue and oven dried at 105 °C for 3 days. Because of their size, the Art Gallery paints were simply mounted on Perspex discs on a thin smear of cyanoacrylate glue. A multi-element analysis was carried out using LA-ICP-MS.

2.2.2. Support mediums

Each paint sample was applied to canvas, watercolour paper and Masonite and when dry, a small sample (5 mm × 5 mm) of the paint on each support was mounted

Table 1
List of paints sampled showing manufacturer and colour

Sample number	Manufacturer	Colour
1	Jo Sonja's Acrylics	Raw umber
2	Atelier Acrylics	Raw umber
3	Mattisse Acrylics	Raw umber
4	Art Spectrum, Oils	Raw umber
5	W&N Oils	Raw umber
6	Oils, Russian	Raw umber
7	Art Spectrum, Water	Raw umber
8	W&N Water Colours	Raw umber
9	Water Colours	Raw umber
10	Jo Sonja's Acrylics	Cadmium yellow light
11	Jo Sonja's Acrylics	Cadmium yellow med
12	Atelier Acrylics	Cadmium yellow light
13	Atelier Acrylics	Cadmium yellow med
14	Art Spectrum, Oils	Cadmium yellow light
15	Art Spectrum, Oils	Cadmium yellow
16	W&N Oils	Cadmium pale
17	W&N Oils	Cadmium yellow
18	Art Spectrum, Water	Cadmium pale
19	Art Spectrum, Water	Cadmium yellow
20	W&N Water Colours	Cadmium pale
21	W&N Water Colours	Cadmium yellow
22	Jo Sonja's Acrylics	Titanium white
23	Jo Sonja's Acrylics	Warm white
24	Atelier Acrylics	Titanium white
25	Acrylics, Russian	Titanium White
26	Art Spectrum, Oils	Titanium white
27	W&N Oils	Titanium white
28	W&N Oils	Zinc White
29	Oils, Russian	Zinc white
30	Art Spectrum, Water	Chinese white
31	W&N Water Colours	Titanium white
32	W&N Water Colours	Chinese white
33	Jo Sonja's Acrylics	Permanent alizarin
34	Jo Sonja's Acrylics	Vermilion
35	Mattisse Acrylics	Alizarin
36	Mattisse Acrylics	Vermilion
37	Art Spectrum, Oils	Alizarin crimson hue
38	Art Spectrum, Oils	Vermilion
39	W&N Oils	Alizarin Crimson
40	W&N Oils	Vermilion hue
41	Art Spectrum, Water	Alizarin hue
42	Art Spectrum, Water	Vermilion permanent
43	W&N Water Colours	Alizarin crimson
44	W&N Water Colours	Vermilion hue

on a Perspex disk using cyanoacrylate glue. A multi-element analysis was carried out using LA-ICP-MS.

The elemental composition of three supports, canvas, watercolour paper and Masonite was also investigated.

2.2.3. Samples of paints from paintings by Kathleen O'Connor

Samples from the works of Kathleen O'Connor were collected by conservators at the Art Gallery of Western Australia using a scalpel and paintbrush while looking through an art conservation microscope. Details of the seven paintings sampled, including the year the work was commissioned (if known), the colour of the sample and the sampling site are given in Table 2.

2.3. Direct analysis

The samples were analysed using an acquisition time of 120 s. The majority of samples were ablated with 10 × 10 grid raster with three shots per site. This represented 300 laser shots per sample ensuring a homogenous signal response was obtained. The samples obtained from the Art Gallery of Western Australia were of an insufficient size and shape to ablate with the 10 × 10 grid raster. The laser was manually moved over the sample with an acquisition time of 40 s. It is essential that the instrument be optimised before any analytical work is carried out. This is achieved by ablating an NBS 610 glass standard at 10 Hz, while adjusting instrument parameters. Analysis of the NBS 610 glass standard is routinely repeated throughout the experiment as a method of monitoring the drift in signal response.

2.4. Indirect analysis

The prototype cell was designed to allow for the sampling of objects larger than the standard ablation cell. The prototype was custom designed to optimise the collection of representative debris, investigating things such as atmosphere, pore size and material of the membrane filter, time of ablation, distance to the holder, power of the applied laser and the mode of the laser used. A detailed description of the prototype and application of the new analytical methodology will be published shortly. However, a photograph of the modified IR laser and diagram of the prototype cell are shown in Figs. 13 and 14.

To determine if the method of sampling is effective for paint substrates, samples of artists paints were ablated using a VG Elemental Nd-YAG laser operating at 10 mJ and a fundamental wavelength of 1064 nm in both free-running and Q-switched operating modes for 2 min each. The debris created was collected inline using a 25 mm membrane filter and an atmosphere of argon flowing through the cell at 0.5 L min^{-1} regulated by a Fisher and Portal flow meter. A new filter was used for each sample and the ablation cell was cleaned with acid and ethanol between each change in sample. The process was the same for both the paints and the 610-glass standard.

One quarter of each of the filters of interest was mounted on Perspex discs using cyanoacrylate glue and analysed using LA-ICP-MS. The samples were each ablated using a 10 × 10 raster with five shots per site. The debris created was purged directly into the ICP-MS for analysis, using argon carrier gas.

3. Results and discussion

LA-ICP-MS is not as yet a reliable, quantitative analytical technique. This is due to the unpredictable nature of ablation where differences in coupling efficiency are caused by differences in sample roughness, co-association of analytes and their chemical form. This leads to differing amounts of material being removed with each ablation event and

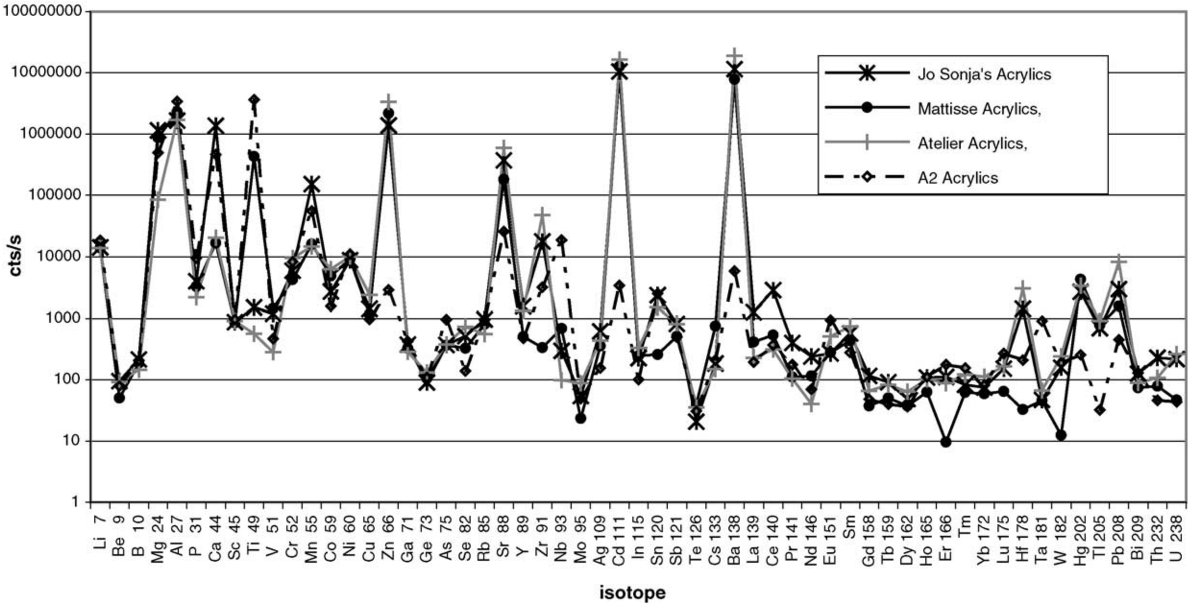

Fig. 1. Cadmium yellow light (in acrylic) from various manufacturers showing variation.

hence differing amounts of analytes are introduced into the plasma. However, the relative amounts of analytes removed are reproducible between lasing events and consequently the comparison of spectral inter-element association patterns, to indicate comparability of samples, is valid. Consequently, an interpretive methodology to compare and contrast elemental spectral patterns, and which can also be used to search a database of fingerprint patterns, is essential for the optimisation and application of the methodology under actual field investigation conditions. Watling et al. [12] have developed a search match protocol used to quickly compare a sample to a database. This method of search/match comparison was used in all paint comparisons in this study.

3.1. Manufacturer differences

As mentioned previously, it is believed that the unique source materials and manufacturing processes undertaken by the manufacturers will lead to differences in the trace element spectral pattern of the subsequent paint products. To investigate this, identically coloured paints from varying manufacturers were analysed and a database of samples established.

The elemental spectral patterns of paints from four different manufacturers of cadmium yellow light are shown in Fig. 1. Whilst there are some similarities between manufacturers (which would be expected as the colour and shade limits the inclusions of elements), the manufacturers are eas-

Table 2
Colour, year and painting source for samples of Kathleen O’Connor’s work

Year	Painting	Sample colour	Year	Painting	Sample colour
Unsure	Still Life with Fish	Green, with yellow	1940	Canterbury Bells	Brown
		Black			Dark brown
		Brown (possibly a mixture of yellow, white and red)			Green, with brown
		Blue			Yellow
Unsure	Italian Model	Blue			Black
		White			Red
		Brown (possibly a mixture of yellow, white and red)			Ground
Unsure	Card Game in Luxemburg Gardens	White	1955	Still Life with Apples	Blue
		Blue			White
		Yellow, with white			Black
		Brown			Yellow
1911	Conversations in Luxemburg	White	1962	Portrait of Sir Russell Dumas	Brown
		Blue, with white			Black
		Blue			White
		White, with yellow			Grey
		Blue			Blue
		Red			

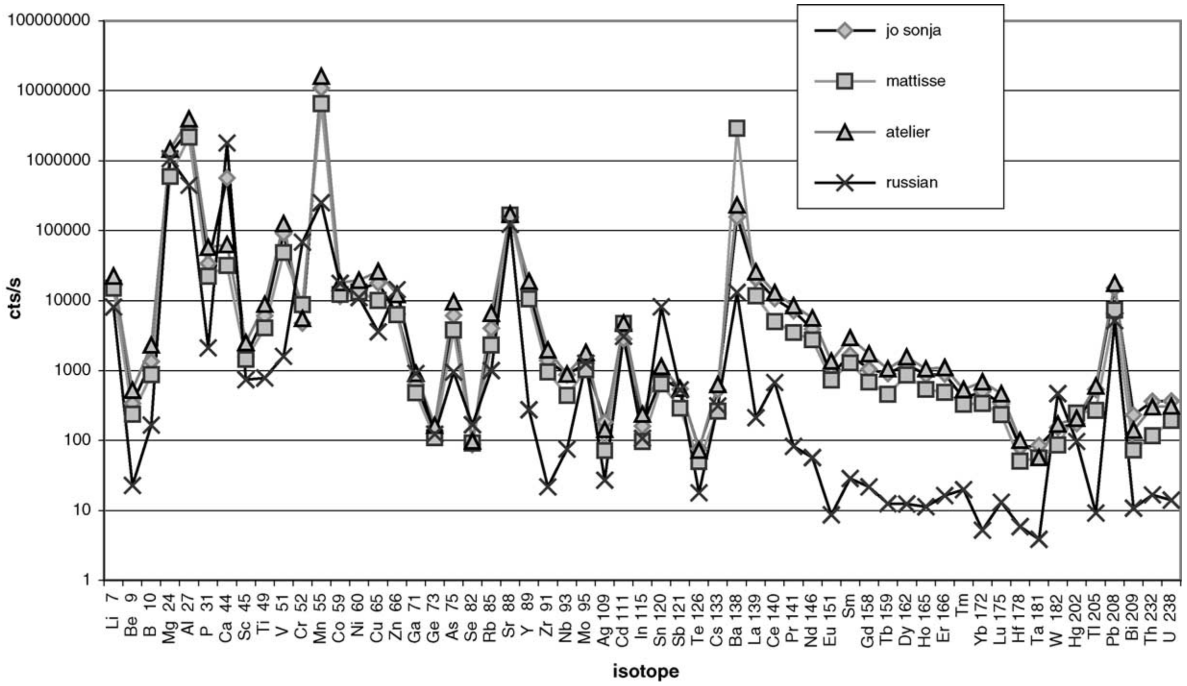

Fig. 2. Raw umber (acrylic) from four various manufacturers showing variation.

ily distinguishable by differences in relative concentrations of the isotopes ^{49}Ti, ^{55}Mn, ^{82}Se, ^{91}Zr, ^{93}Nb, ^{120}Sn, ^{181}Ta and ^{208}Pb.

The comparison of the trace element profiles for three manufacturers of raw umber paint (Fig. 2) shows variation like that of the cadmium yellow light in Fig. 1. There are differences in relative concentrations of ^{52}Cr, ^{55}Mn, ^{91}Zr, ^{138}Ba and ^{182}W. Whilst there is more similarity in patterns between the Atelier, Jo Sonja and Mattisse profiles in comparison with the Russian profile, possibly suggesting similar manufacturing processes, the three can be distinguished based on concentrations of ^{24}Mg, ^{27}Al, ^{65}Cu, 75As, ^{91}Zr, ^{138}Ba and some of the rare earths.

3.2. *Effect of substrate*

As the sampling of the artwork does not always permit the collection of a clean paint fragment without any contamination from the backing material, a study of the effect of the backing on the elemental spectral profile was undertaken. A comparison of Art Spectrum alizarine oil on canvas, paper and Masonite is shown in Fig. 3.

The similarities between the three are easily apparent. However, some elements are enriched in the substrates potentially making comparison more difficult. Masonite is enriched in ^{208}Pb, and paper is enriched with ^{138}Ba due to the $BaSO_4$ filler used in the paper. However, even with these enrich-

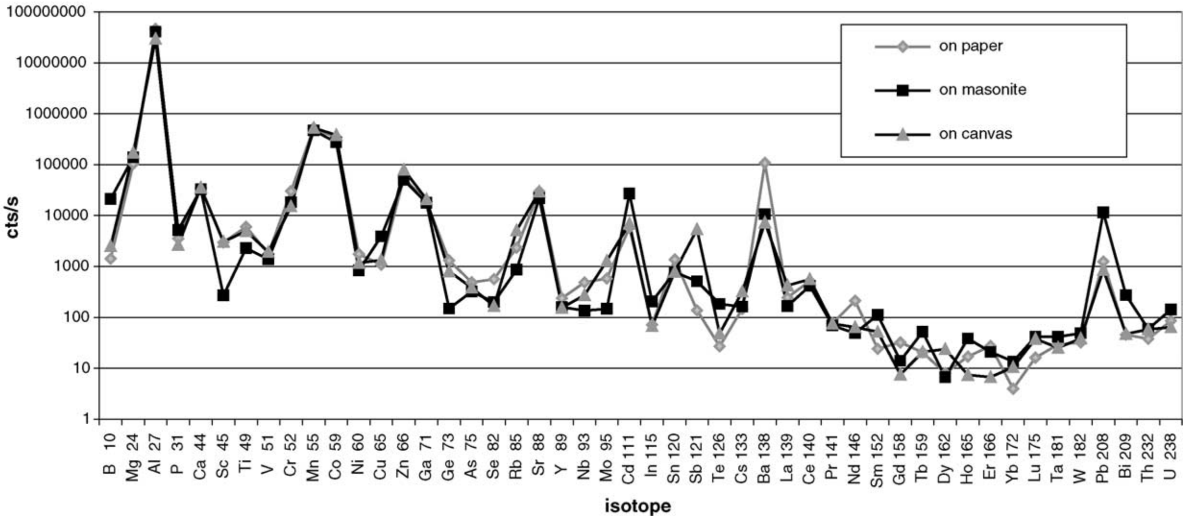

Fig. 3. Art Spectrum alizarine crimson oil paint on the three substrates, showing similarities between the three.

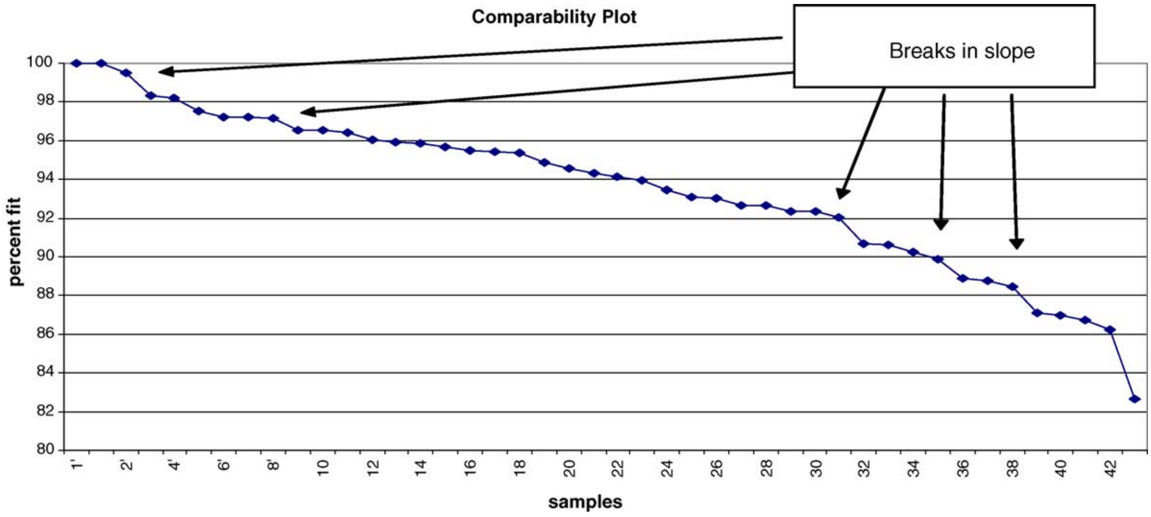

Fig. 4. Database search/match comparability fits for Art Spectrum, watercolour, vermilion, on canvas.

ments, the trace element distribution pattern of the paint is apparent and unambiguous. The substrate of the painting is easily recognised and hence is easily corrected for when searching a database, as it simply requires searching a database based on elemental profiles obtained from samples mounted on the specific substrate in question.

Fig. 4 illustrates the numerous breaks in slope present in the reduced comparability percent index plot of the search/match for Art Spectrum Vermillion, watercolour on canvas, and the table of the first 20 matches for the plot are shown in Table 3. The comparability index statistics used for the plot are based around a sorting sub-routine that identifies the logarithmic values of the raw count data and compares these with equivalent element values in the remaining database samples. These differences are then summed and sorted to obtain an approximation of the comparability of the spectra. The series is sorted on the basis of the difference from a 100% fit of the questioned sample with itself. A 100% fit can only be achieved with absolutely identical spectra being compared, a situation which will never exist in a chemical analysis and is only possible by duplicating the questioned sample in the database. The 100% fit ensures that the maximum possible comparability point is fixed in the interpretational protocol and obviously both the top and the bottom database fits are artificial but give a good idea of the “fit” of the spectres. In addition to simply referring to the numbers (percentage comparability), it is also advisable to plot the percentage comparability relative to the specific

Table 3
Percentile comparability table of first 20 fits to Art Spectrum Vermillion* watercolour on canvas as based on search of canvas database

Ranked match	Manufacturer	Colour name	Percentile comparability
1	Art Spectrum*	Vermilion	100
1	Art Spectrum	Vermilion	100
2	Art Spectrum	Alizarin crimson	99.49655255
3	Matisse	Alizarin	98.30507976
4	Matisse	Vermilion	98.20844663
5	Russian	Raw umber	97.51947032
6	Jo Sonja	Vermilion	97.2168847
7	Jo Sonja	Cadmium yellow light	97.1927896
8	Winsor and Newton	Raw umber	97.14578271
9	Jo Sonja	Warm white	96.55888532
10	Jo Sonja	Permanent alizarin	96.55262544
11	Jo Sonja	Cadmium yellow medium	96.44801434
12	Jo Sonja	Titanium white	96.05103102
13	Art Spectrum	Raw umber	95.93818795
14	Matisse	Raw umber	95.85073238
15	Winsor and Newton	Titanium white	95.6783539
16	Winsor and Newton	Alizarin crimson	95.51642509
17	Atelier	Raw umber	95.43108123
18	Atelier	Cadmium yellow light	95.36495223
19	Jo Sonja	Raw umber	94.85936493
20	Winsor and Newton	Alizarin crimson	94.54956608

sample giving that comparability and its positional number in the database. In this way, significant “breaks in slope” in the plot can be observed. These phenomena usually indicate the start of new populations and are a means of sorting data and speeding up the comparison process, after which the spectres of those closest fitting to the questioned sample are visually compared to ensure that the fit is genuine and not an artifact based on only statistics.

3.3. *Effect of binder*

The effect of the binder used in the manufacture of the paint was also investigated. The trace element profiles of Art Spectrum raw umber manufactured with oil or watercolour binders are shown in Fig. 5. The same manufacturer and same pigment colour should mean that any differences are due to the manufacturing process unique to the binder used. Whilst the two are very similar there are some minor differences in their elemental spectral patterns associated with ^{51}V, ^{52}Cr, ^{60}Ni, ^{120}Sn, ^{126}Ta, ^{182}W. However, these differences are not significant enough to produce a mismatch with another manufacturers colour or even another manufacturer as shown by the differences between the two and the different manufacturer of raw umber oil at isotopes of ^{27}Al, ^{51}V, ^{60}Ni and ^{111}Cd.

3.4. *Kathleen O’Connor samples*

Samples from paintings by Western Australian artist, Kathleen O’Connor, were used to create a database consisting of analytical data for paintings from 1911 to 1962 as well as three paintings of which the dates of commission were unknown. The paintings sampled, their dates of commission and colour of the sample taken are listed in Table 2.

In the establishment of a reference database for all pigments, it is possible to ablate the reference samples for a prolonged time and thereby obtain meaningful data for trace and ultra-trace levels of the elements present. This ensures that the database is as comprehensive as possible. This situation is not always possible when analysing paintings. The reasons for this are two-fold. Firstly, excessive ablation may lead to artistically unacceptable damage of the painting. Secondly, an artist’s technique will often lead to overlap of colours resulting in areas of mixed pigment. Therefore, it is necessary to select areas where it is obvious that only one specific pigment has been used and these are often small and well defined. Ablation of these areas will ensure that only one single pigment is analysed and an unambiguous element fingerprint obtained. Ablation of a smaller area will lead to reduced sensitivity and may lead to an incomplete fingerprint being obtained where possibly only elements contained in trace and minor concentrations will be represented. However, it is still possible to compare these trace and minor element concentrations with equivalent elements in database samples to obtain an unambiguous match. Additionally, if larger areas of single pigment can be found, and these can be ablated without visible damage to the painting, it will be possible to use these to compare to the total element fingerprint as recorded in the database. Combinations of these two ablation protocols, combined with the database search protocol, will ensure optimum comparison and identification of pigments on paintings is achieved.

The painting entitled ‘The Italian Model’ was painted on the back of ‘Card Game in Luxemburg Gardens’ suggesting that possibly these were completed within a relatively small time frame. The exact dates of commission for these paintings are unknown. However, from historical knowledge, it is known that they were completed during the artist’s time in Luxemburg and as such are likely to be from approximately the same time period as the painting entitled ‘Conversations in Luxemburg Gardens’ completed in 1911. Consequently, it is possible that the same painting materials would have been used for all three paintings and this would be reflected in the element profiles of the samples taken and as such narrow

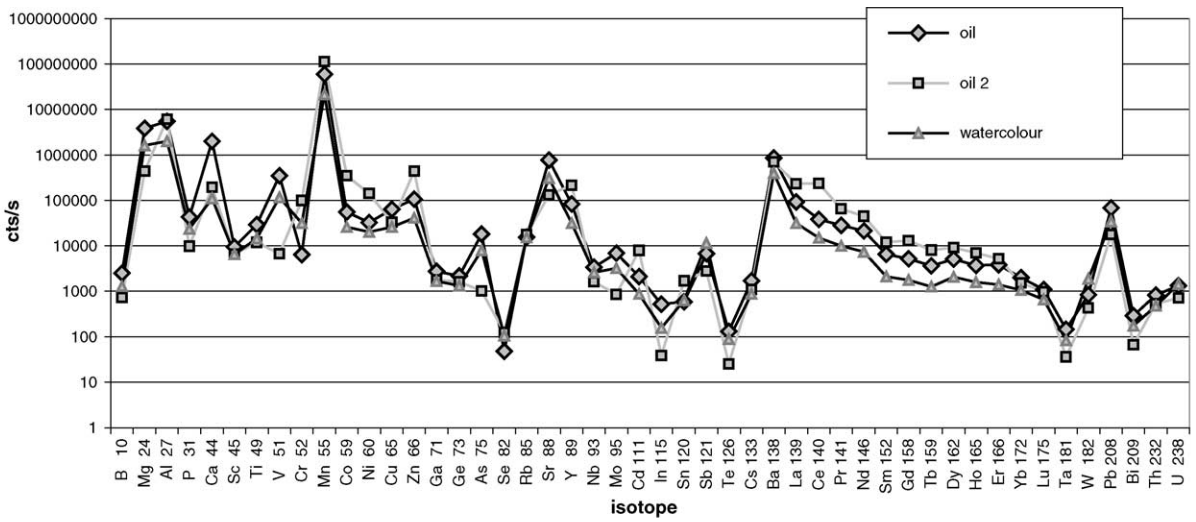

Fig. 5. Art Spectrum raw umber oil and Art Spectrum raw umber watercolour both on canvas in comparison with raw umber (oil 2) from another manufacturer.

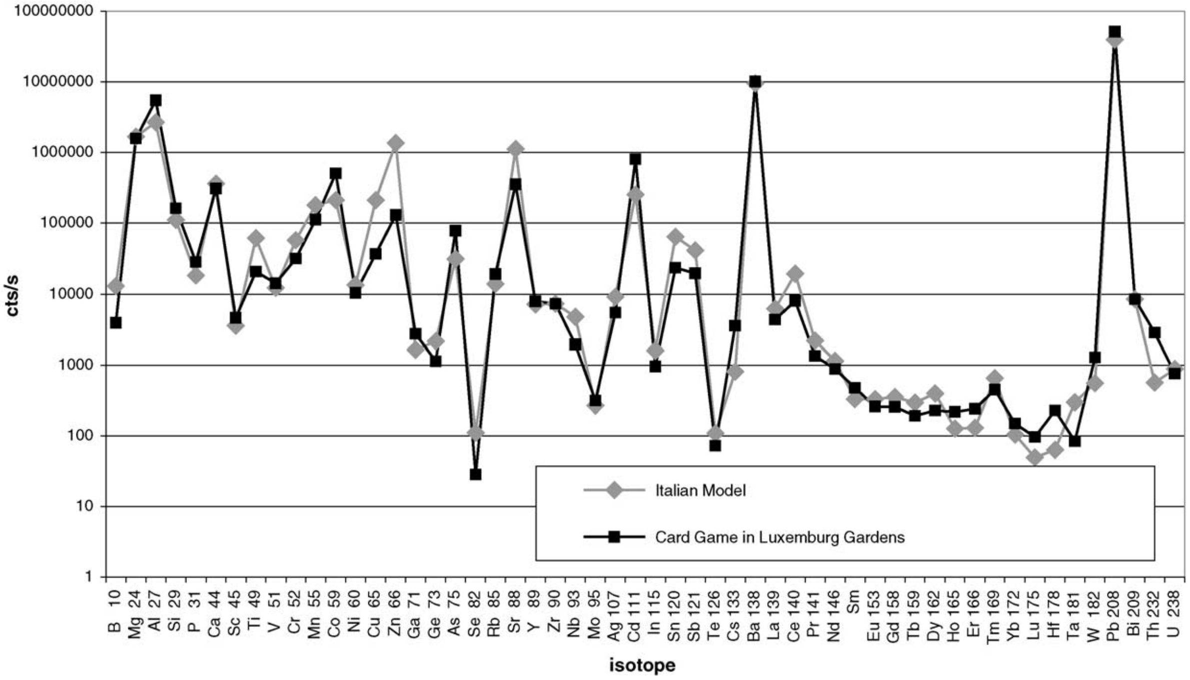

Fig. 6. Logarithmic plot comparing the element profiles of brown paints taken from separate paintings.

down the time frame from which these two paintings were completed.

The element profile of a brown paint sample taken from ‘The Italian Model’ was compared to other samples within the database. The closest match, with a 96.2% fit, was the element profile of a brown paint taken from ‘Card Game in Luxemburg Gardens’. Fig. 6 illustrates the remarkable similarity between the element profiles. While the element profiles show a high degree of correlation, some differences are noted between ratios of ^{49}Ti, ^{59}Co and ^{66}Zn. The differences between these elements may be a result of contamination by another coloured paint. ‘The Italian Model’ painting has higher levels of cobalt than ‘The Card Game in Luxemburg Gardens’, which could be due to inclusion of some of the blue paint in the sample analysed. The element composition would be altered slightly depending on the quantity of the ‘unknown’ paint in the mixture. Even with these factors considered, the element profiles of the two brown paints are of such similarity to suggest they are from the same pallet.

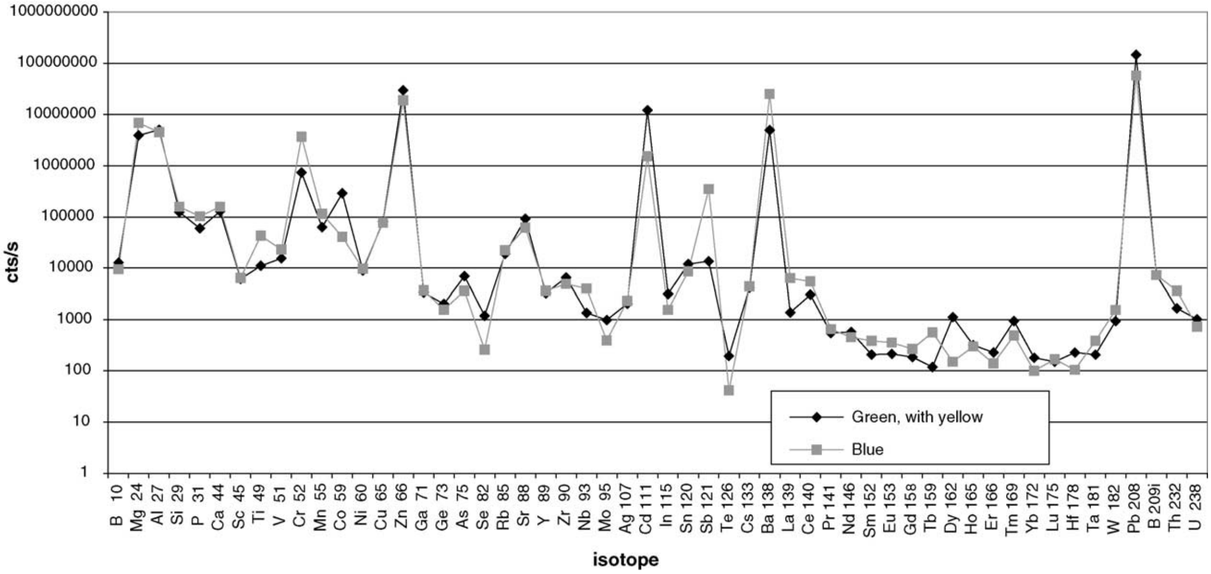

Fig. 7. Logarithmic plot comparing the element profiles of blue and green, with yellow, from ‘Still Life with Fish’.

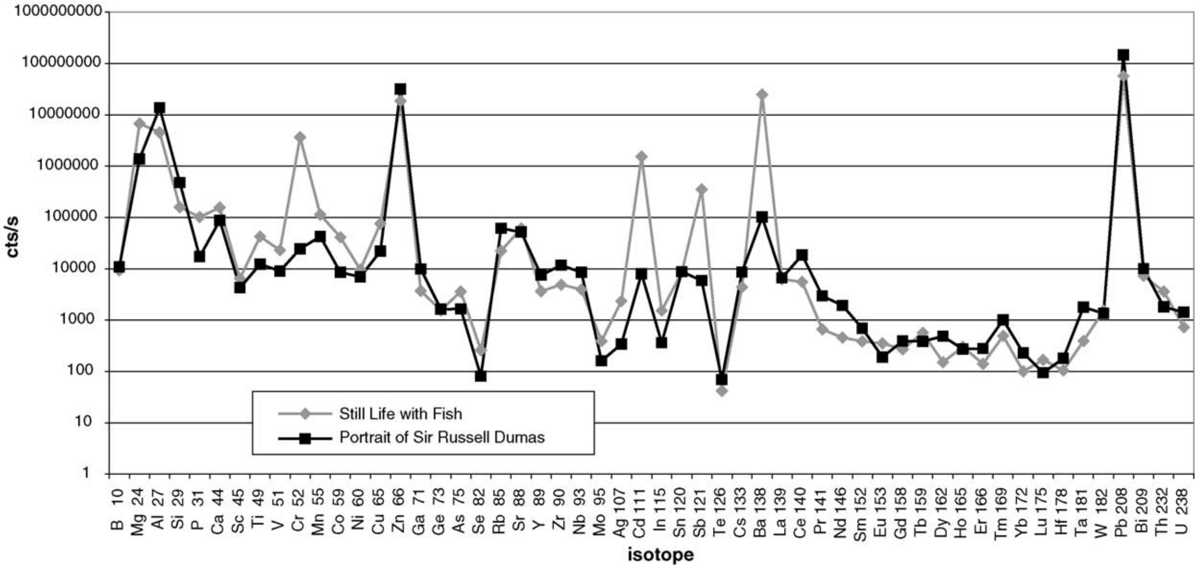

Fig. 8. Logarithmic plot comparing the element profile of blue from ‘Still Life with Fish’, to blue from ‘Portrait of Sir Russell Dumas’.

The same analytical protocol was followed to search and compare the element profiles of the remaining samples. Fig. 7 illustrates the element composition of a ‘blue’ sample and a ‘green with yellow’ sample. The element profiles have a high degree of similarity. However, differences are noted between relative ratios of ^{49}Ti, ^{59}Co and ^{121}Sb. The green sample is likely to be a mixture of blue and yellow and as such its element composition will be similar to the blue paints element composition. The differences noted are likely to be from the contribution to the element profile by the element composition of the yellow paint. However, the two element profiles in Fig. 7 are very close, which suggests that mixtures of paint can be used in provenance establishment studies. Further investigation needs to be carried out on the effect of mixtures on the combined element profiles of the sample.

The element profile of a blue paint sample taken from ‘Still Life with Fish’ was compared to other samples within the database. The closest match was the element profile of a blue sample from ‘The Portrait of Sir Russell Dumas’. The similarities are illustrated in Fig. 8.

The element profiles are exceptionally close, with differences limited to relative levels of chromium, cadmium, antimony and barium. The blue paint from ‘Still Life with Fish’ contains much higher levels of these four elements.

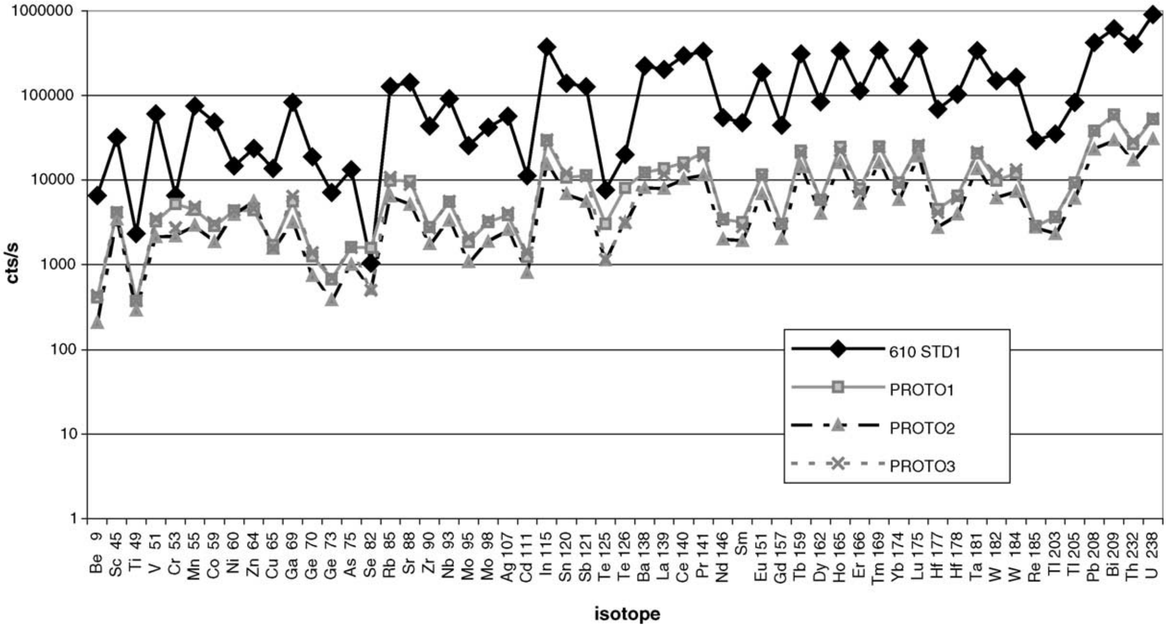

Fig. 9. Log plot of glasses with prototype showing reproducibility of pattern.

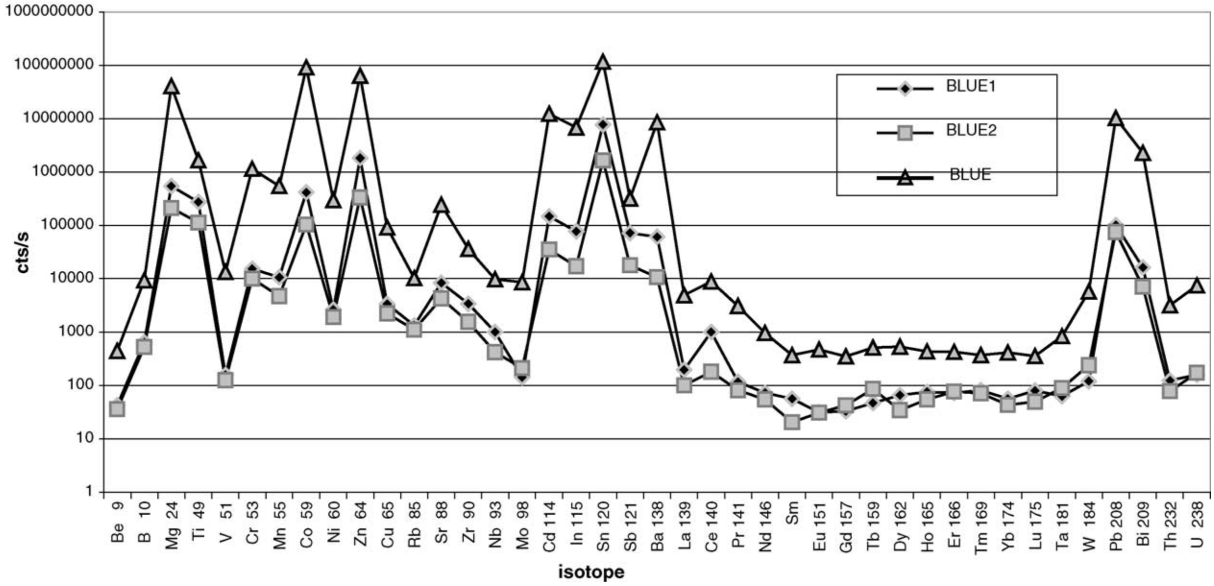

Fig. 10. Comparison of the ablation directly of scraping of blue paint analysed directly and the ablation and collection in situ of the same blue paint (in duplicate) using prototype.

However, as previously detailed, the blue paint is high in cadmium and barium due to ‘contamination’ from the element profile of the yellow paint present in ‘Still Life with Fish’. Consequently, these three elements can be excluded from the comparison. The residual element profiles are essentially the same suggesting that the paints are from the same pallet. The element profile of the blue sample did not exhibit the same degree of similarity with any other sample in the database. It is therefore probable that ‘Still Life with Fish’ was painted during the 1960s (‘Portrait of Sir Russell Dumas’, commissioned 1962), and is unlikely to predate 1955 (‘Still Life with Apples’, commissioned 1955).

3.5. *In situ analysis of paintings*

In all of the previously mentioned analysis, samples had to be removed from the painting with a scalpel, risking damage to the artwork and contamination of the paint flake. Therefore, a method of sampling the painting without the need to cut out flakes needs to be developed. The device proposed will allow for the direct analysis of samples of paint in the painting of interest with minimal damage. The stage was removed and replaced by a manual stage and adaptations made to incorporate the prototype cell.

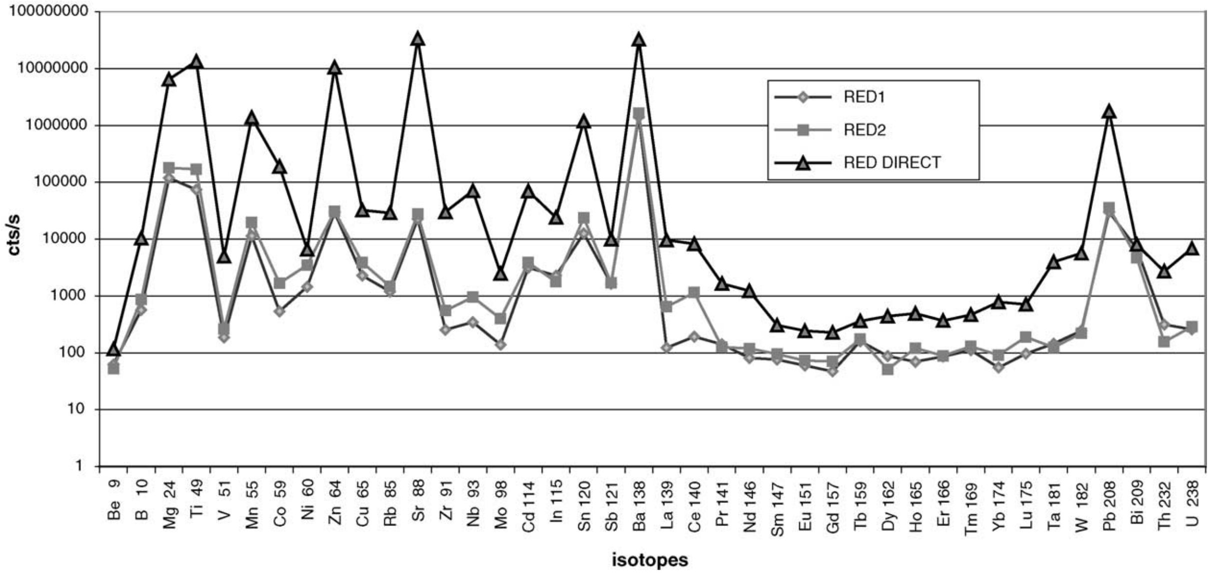

Fig. 11. Comparison of the ablation directly of scraping of red paint analysed directly and the ablation and collection in situ of the same red paint (in duplicate) using prototype.

To establish if the prototype design is able to sample in an open cell, a NIST standard glass (NIST 610) was used to test the prototype. Fig. 9 shows the logarithmic plot of the element profile of three repeats of the standard ablated using the IR laser and collected on filters, then re-ablated and analysed using LA-ICP-MS. These three samples are compared with the direct analysis of the glass standard using LA-ICP-MS (labelled 610 std1). The match of the pattern is clearly visible as all four plots follow the same trend. The reductions in sensitivity of some of the samples are due to the differing coupling efficiencies as mentioned previously. However, even with the differences, the patterns are still visible and the samples collected and analysed are just over 100 times lower even though only a 350th of the filter is ablated by the 15 × 15 raster used.

The trace element profiles of the analysis of the scrapings of blue paint directly by LA-ICP-MS and the analysis of the collected debris created by the prototype ablation of the same area of blue paint from "untitled" by Francis Ryan, 2003 is shown in Fig. 10. Whilst again the reduction in counts is seen due to differences in coupling efficiency and the dilution due to the collection by the filters and limited time of ablation, the three patterns are notably similar.

The trace element profiles of the analysis of the scrapings of red paint directly and the analysis of the collected debris of the same area of red paint from "untitled" by Francis Ryan, 2003 is shown in Fig. 11. The patterns are not as similar as the blue paint is, as some differences are seen at ^{24}Mg, ^{60}Ni and ^{209}Bi; however, the technique still offers a representative sampling technique.

The two paints (red and blue) also can be easily distinguished elementally from each other by the ratios of ^{120}Sn to ^{208}Pb, ^{88}Sr to ^{91}Zr and the concentrations of ^{138}Ba, ^{88}Sr, ^{59}Co and ^{91}Zr.

4. Conclusion

Overall, this study has shown the possibility of using the trace elements to help aid in the detection of forgeries or the authentication of questioned artworks based on comparison with known works and materials. Different manufacturers were investigated and were found to be distinguishable even within the same pigment and binder combination. The binder and the substrate may have an effect on the fit of the database search and so should be accounted to limit the effect. Three undated artworks by Kathleen O'Connor were sampled the comparisons with known works indicated the possibility of the same palette for the blues from "Still Life with Fish" and "the Portrait of Sir Robert Dumas" (commissioned 1962) and hence the two can be dated as being painted around the same time.

A prototype device for the in situ sampling of objects larger than a standard ablation cell was used to ablate and collect samples of the blue and red paint from Francis Ryan's untitled 2003 work. On comparison with scrapings of the paint analysed using standard LA-ICP-MS, the proposed application of the device as an alternative method of sampling artworks is supported.

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