

# ANALYSIS OF INORGANIC MATERIALS FROM PAINTINGS AND WATERCOLOURS BY PAUL CÉZANNE FROM THE COURTAULD GALLERY USING TWO METHODS OF NON-INVASIVE PORTABLE XRF WITH LIGHT MICROSCOPY AND SEM/EDX SPECTROSCOPY

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## ABSTRACT

*The inorganic materials used by Paul Cézanne for six paintings and five watercolours from the Courtauld Gallery, London have been examined using two kinds of portable X-ray fluorescence (XRF) equipment and IR reflectance spectroscopy, and analysis of paint samples using Light microscopy (LM) and SEM-EDX. The aim of the study was to define parameters for identification of inorganic pigments, extenders and preparation layers in the works, and to assess the resolution and reliability, advantages and shortcomings of the portable techniques by comparison with sampling methods. Results of the analysis of a painting The Montagne Sainte-Victoire c1887, and a work on paper Apples, Bottles and Chair Back 1904-1906 are given. XRF using both types of equipment was useful for the characterisation of some of the inorganic materials used for works on canvas, and in particular the watercolour on paper, where it was not possible to take samples for SEM/EDX or other techniques. For the painting, XRF data required complimentary data from LM and SEM/EDX for characterisation of the inorganic materials in mixtures or layers, while XRF with LM was sufficient for characterisation of the inorganic materials in the watercolour where pigments were used unmixed and in a single layer.*

## INTRODUCTION

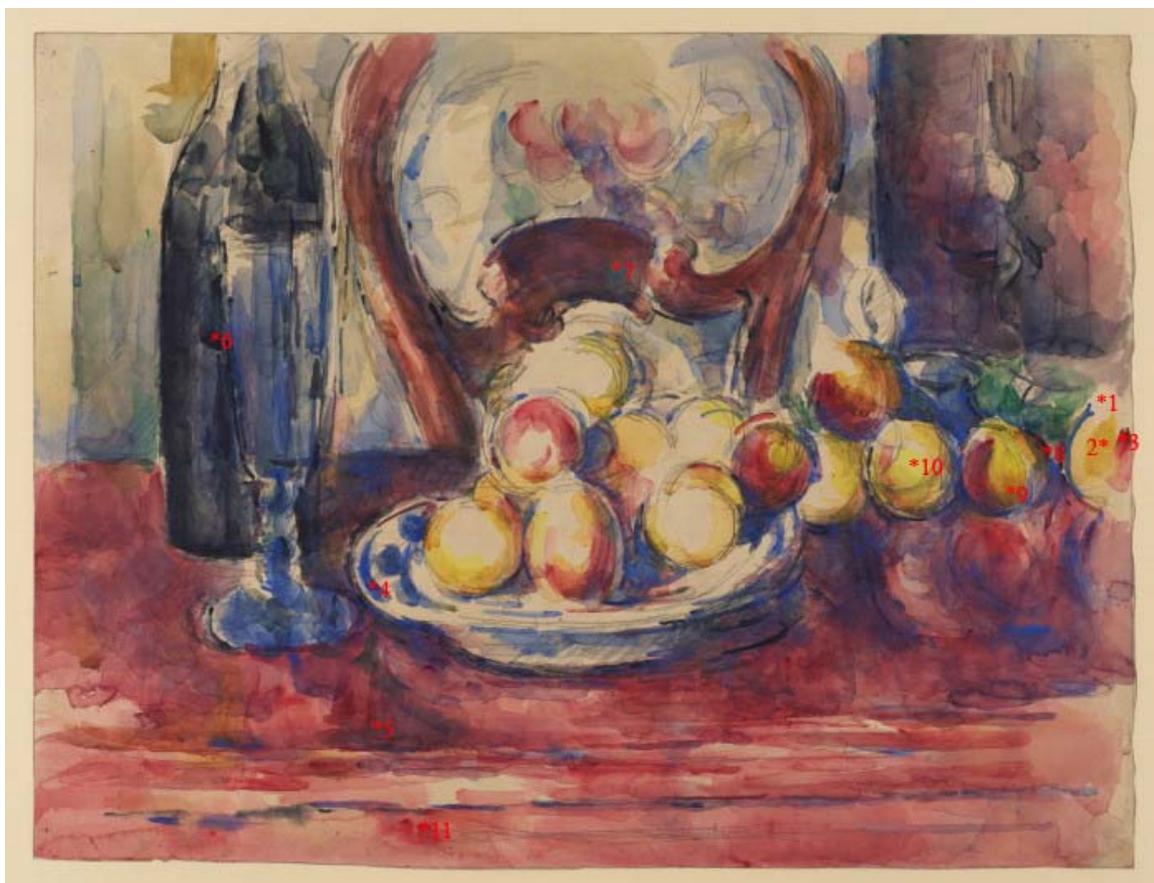
A technical and historical study of paintings and works on paper by Paul Cézanne (1839-1906) in the Courtauld Gallery included characterisation of pigments used for the works using a combination of non-invasive analysis using two kinds of portable XRF equipment. XRF has been widely applied for the characterisation of inorganic materials in works of art, with more recent developments in the technology providing portable easy to use equipment that has facilitated the use of the technique by conservators (see for example Ferretti 2000). In the present study identification of pigments and inorganic materials was based on deduction from elemental analysis using XRF, using portable equipment used by the MOLAB group, and with a handheld Bruker portable XRF instrument. The MOLAB instrument allows the detection of elements with atomic number higher than silicon ( $Z > 14$ ). The Bruker AXS instrument is capable of potassium ( $Z = 19$ ) and higher, whereas flushing with helium allows for detection of elements down to Al ( $Z = 13$ ).

Where possible, a sample was prepared as cross-sections for characterisation of the preparation layers and inorganic pigments using LM and SEM/EDX that provided data on the optical characteristics of the materials and spatially resolved elemental analysis. This could be used to interpret data obtained using the non-sampling analytical methods. Layer-specific characterisation of the painted works was limited by the opportunity to take samples whilst the works on paper provided no opportunity for sampling.

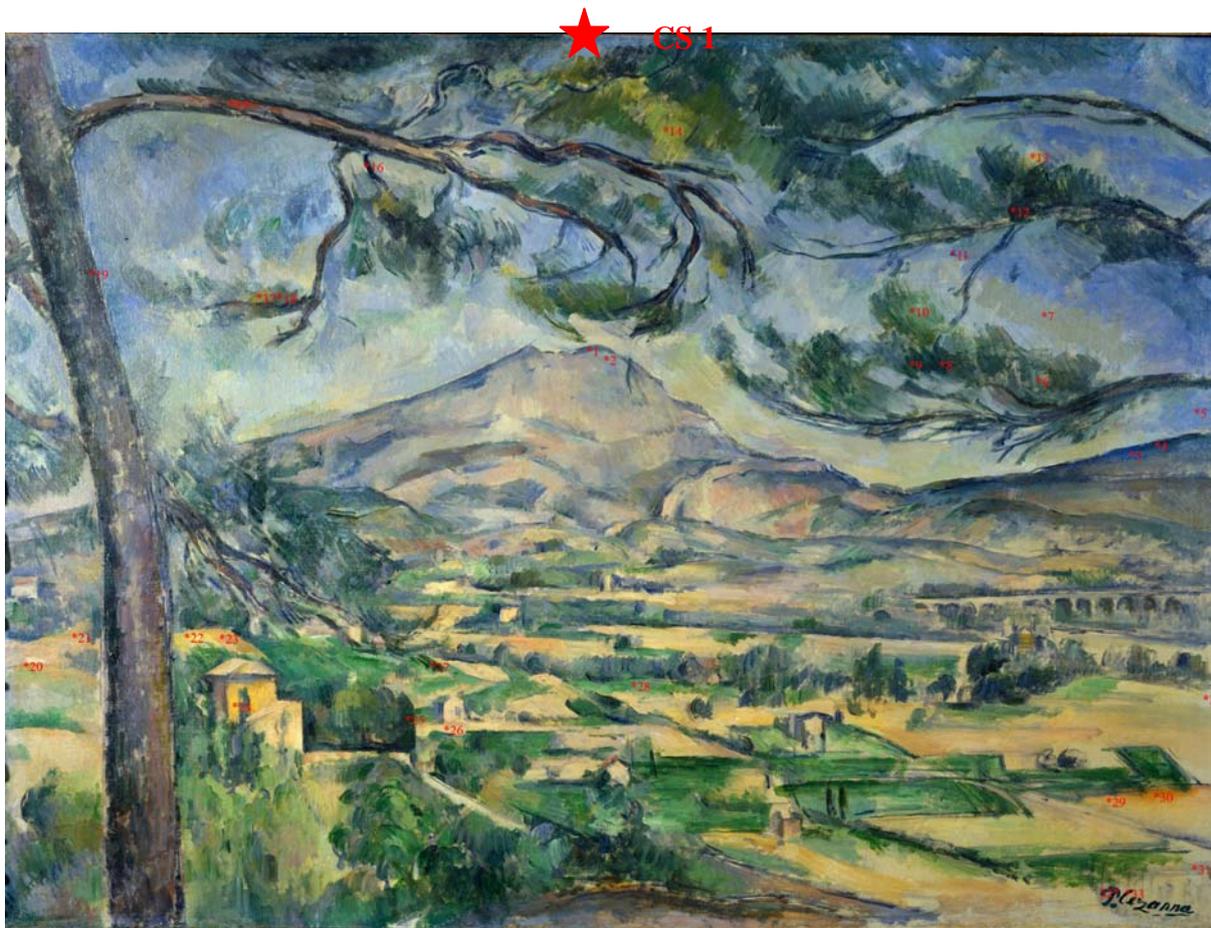
The results of the study of this group of works are described more fully in a forthcoming exhibition at the Courtauld Gallery and the accompanying exhibition catalogue *The Courtauld Cézannes* (Reissner 2008). This paper focuses on the practical aspects of the analytical

challenges posed by a limited group of post-Impressionist works by Cézanne, and an assessment of the advantages and limitations of the analytical techniques used to identify the inorganic materials used by the artist.

### The Work on Paper and Painting by Paul Cézanne



*Fig 1 Apples, Bottles and Chair Back 1904-1906. Pencil, watercolour on paper 45.8 cm x 60.4 cm Samuel Courtauld Gift; 1948, showing sites analysed by XRF.*



*Fig 2 The Montagne Sainte-Victoire c. 1887 oil on canvas 66.8 cm x 92.3 cm Samuel Courtauld gift; 1934. Areas analyzed by XRF and sample site for paint-cross section 1 are marked on the image.*

### **ANALYTICAL PROCEDURES**

The MOLAB equipment was part of a mobile laboratory accessible to European scientists through the Eu-ARTECH project, funded by the 6<sup>th</sup> Framework Program. X-ray fluorescence (XRF) spectra were recorded using portable equipment made with a miniaturised x-ray generator EIS P/N 9910, equipped with a tungsten anode and a silicon drift detector (SDD) cooled with a Peltier element. The SDD has a resolution of about 150 eV at 5.9 keV. The portable instrument allows the detection of elements with atomic number higher than silicon ( $Z > 14$ ). The excitation parameters used during the investigations were: voltage of 38 kV and current of 0.05 mA. The XRF instrument provided by MOLAB group delivered and detected fluorescence via a detector placed millimetres from the painting surface (Fig 3a). The acquisition time was 120 seconds for the painting and 400 seconds for the watercolour. The distance sample-detector was fixed at 2 cm. The beam diameter under these conditions is 4 mm. Spectra were interpreted by specialists in the MOLAB team, and their use of multivariate statistical analysis of data from the non-invasive XRF and FTIR analysis of two paintings in the Courtauld Gallery by Cézanne is published elsewhere (Rosi et al. 2008).

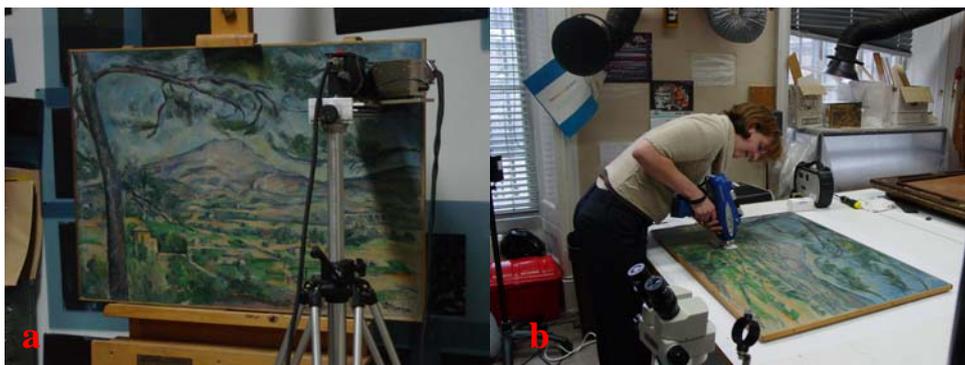


Fig 3a XRF analysis of painting using MOLAB equipment and 3b Bruker Tracer

Further analysis was undertaken with a Bruker AXS KeyMaster Technologies Tracer III-V Portable Light Element XRF Analyzer (Tracer), loaned to the Courtauld Institute of Art by the manufacturer (Fig 3b). The instrument has three standard settings: 40kV, 1.5 $\mu$ A; 33kV, 1.2 $\mu$ A; 15kV, 15 $\mu$ A. The latter two settings are used with the instrument sensor under vacuum. The lower energy settings were more appropriate for decreasing atomic weight elements, and the lightest detectable element is aluminium. The results are not quantitative, as peak heights will vary according to the x-ray conditions and atomic weight. The detector is less sensitive to light elements. The Tracer instrument was padded away from the paint surface using a piece of non-woven felt with a target hole cut out, which cushioned the metal edges of the instrument away from the picture, whilst only increasing the sensor distance from the surface by 1mm. A piece of Melinex film was placed over the sensor to protect it against dust ingress. The acquisition time was on average 20 seconds. The best data were obtained from the works on canvas placed flat on a table top and supported from behind (Fig 3b). For the analysis of the works on paper, a similar strategy was used. The beam diameter under these conditions is approximately 5mm.

Spectra were output to both a handheld PDA and to a laptop computer, and peaks could be labelled using the accompanying software. Subsequent interpretation of data was undertaken by Courtauld Institute staff following guidelines provided by the manufacturer, but with little experience of the technique.

Using both the XRF equipment types it was possible to gather data from any point on the painted surface, and to compare data gathered from areas of unpainted exposed under layers of ground, or from the edge of the paper support. This was critical in interpreting the elemental data gathered from painted passages that derives from an area of unknown three-dimensional spatial resolution, as commonly the ground materials would be detected. Interpretation could be further enhanced by concurrent study with cross sections to examine layer structure. It was possible to take only a few samples from the edge of the work on canvas described in this paper, and no samples could be taken from the work on paper.

A sample (CS1 in Fig 1) was taken from the edge of the painting of *The Montagne Sainte-Victoire* from an area of blue sky, using a scalpel under low powered microscope, and embedded in Metset® polyester/styrene resin. Samples were subsequently photographed using a SLR digital camera attached to a Leica Aristomet light microscope and carbon coated for analysis using an Oxford Instruments light element EDX detector attached to a JEOL S100 Scanning electron microscope.

## RESULTS

### *Apples, Bottles and Chair Back*

Using both the Tracer and MOLAB equipment spectra were gathered for the unpainted paper, as a reference for the subsequent interpretation of the painted areas (See Fig 1; Table 1 for XRF results). Both XRF techniques detected major peaks for iron and calcium. Minor peaks were detected for chrome, manganese and strontium using the MOLAB equipment, which in general produced spectra with a better signal-to-noise ratio (most likely as a result of relatively high power and longer acquisition times).

<i>Site</i>	<i>Site description</i>	<i>Elements MOLAB XRF</i>	<i>Elements Tracer</i>
1	Paper	Ca (Cr) (Mn) Fe (Sr)	<u>Ca</u> <u>Fe</u>
2	Yellow	Ca (Ti/Ba) Cr (Mn) <u>Fe</u> (Hg?) Pb (As?) (Sr)	
3	Red	<u>Ca</u> (Cr) (Mn) <u>Fe</u> (Pb) (Co) (Sr)	
4	Blue	Ca (Cr) (Mn) <u>Fe</u> <u>Co</u> (Sr)	Al <u>Ca</u> <u>Fe</u> <u>Co</u>
5	Purple	(S) Ca (Ba) (Cr) (Mn) Fe Co (Cu) (As) (Sr)	
6	Dark blue	(S)(K) <u>Ca</u> (Cr) (Mn) <u>Fe</u> Co (Sr)	
7	Dark Green	(S) <u>Ca</u> (Ba) (Cr) (Mn) (Fe) Co Cu As (Sr)	<u>S</u> (Ca) <u>Fe</u> <u>Cu</u> <u>As</u>
8	Red	(S) <u>Ca</u> (Ba) (Cr) (Mn) <u>Fe</u> Co (Pb) (Sr)	
9	Dark Yellow	(K), Ca Cr Fe (Co) Pb (Sr)	
10	Yellow	<u>Ca</u> Cr Fe Pb (Sr)	
11	Red	(K) Ca (Cr) (Mn) Fe (Sr)	

*Table 1. XRF analysis results of Apples, Bottles and Chair Back using MOLAB equipment. Site location see Fig 1. Acquisition time 400 sec.*

The Tracer instrument was used to examine two further areas on the watercolour. In a blue passage the instrument identified the presence of cobalt and aluminium using the 15kV, 15µA settings with the sensor under vacuum, suggesting the presence of cobalt aluminate blue, or possibly a mixture of cobalt blue and ultramarine. Peaks corresponding to iron and calcium were also detected. The possible presence of Prussian blue, indicated by the peak for iron, could not be confirmed with this analytical technique, as this peak could be simply related to the paper substrate, but subsequent FTIR analysis by MOLAB detected the use of indigo for the darkest blue paint passages in this work.

The MOLAB equipment was used to examine two blue passages of paint and similarly detected principal peaks for cobalt, calcium and iron, although aluminium could not be detected. Again, minor peaks corresponding to chrome, manganese and strontium were detected, and could be attributed to elements present in the paper support. In one area further minor peaks were detected for sulphur and potassium, which could possibly be attributed to the presence of additions of other inorganic materials to the blue pigment.

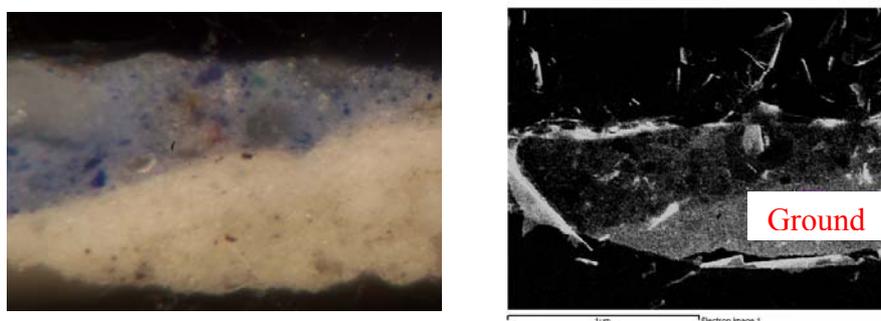
The second painted area examined with the Tracer instrument was from a bright green paint passage, and spectra were gathered under two different conditions: 40kV, 1.5µA and 33kV, 1.2µA, the latter under vacuum. Well resolved spectra were produced, giving clear major peaks for copper and arsenic, suggesting the presence of emerald green. As before, calcium and iron peaks were detected, but appeared as minor peaks on the spectra, as the capture conditions were weighted towards heavier elements. In a green passage examined by the MOLAB instrument, copper and arsenic were similarly detected, with an additional major

peak for cobalt, suggesting that in this instance the green was modified with the addition of cobalt blue, or that a cobalt blue passage lay beneath the upper layer of emerald green.

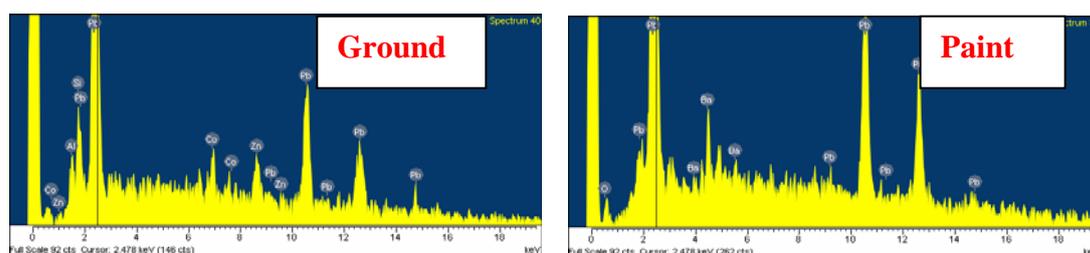
Additional sites were examined with the MOLAB XRF equipment, identifying chrome and lead in yellow passages, suggesting lead chromate. In red passages the results were more difficult to interpret, as the principal peaks corresponded to elements Fe and Ca that were detected in the unpainted areas of paper, although cobalt was detected as an additional peak in some instances.

### ***The Montagne Sainte-Victoire***

A paint sample from the blue sky of this painting was used to give spatially resolved elemental data to compare to the XRF data undertaken using both the MOLAB (See Table 2) and Tracer equipment. Fig 4a illustrates the paint cross-section photographed using the light microscope. The same sample was subsequently prepared for EDX analysis and selected spectra derived from point analysis of the sample are given in Fig 5.



*Fig 4a LM image (800x) Cross section from blue sky from of The Montagne Sainte-Victoire ( from site CS 1 in Fig.1) showing a mixture of cobalt and French ultramarine blue, emerald green and white pigments applied over white ground. 4b shows a backscattered electron image of the cross section prepared for SEM/EDX analysis.*



*Fig 5 EDX analysis of the ground and paint layers from the CS1 from the sky of The Montagne Sainte-Victoire.*

Using LM the layer structure of the painting could be described and most of the pigments assigned tentatively by their optical characteristics, and identification was supported by elemental analysis (Fig 5). The single layer of (commercially prepared) white ground comprises a mixture of barium and lead that is indicative of lead carbonate and barium sulphate. A wet in wet mixture of pigments used for the sky include elemental cobalt and aluminium, corresponding to characteristic violet-blue particles of cobalt aluminate, in a matrix of white pigments containing elemental lead, zinc and barium. It could be deduced that the white pigment is likely to comprise a mixture of lead carbonate with either barium sulphate or lithopone (barium sulphate with zinc sulphide) or alternatively, zinc oxide may be present. French ultramarine, evident in the upper part of the paint layer characterised in the light microscope by small (1-5 $\mu$ ) rounded deep blue particles in the light microscope gave elemental spectrum that included aluminium, silica and sulphur (derived from a peak overlap

with the  $K\alpha$  peak for Pb) in the white matrix containing lead carbonate. The absence of elemental sodium that characterises the sodium aluminium silicate pigment may be due to its relatively low concentration and low sensitivity of the detector for this element.

Analysis of blue paint passages using the XRF equipment can be compared to the results from the cross section, particularly site 5 of the MOLAB XRF survey (Fig 2, Table 2). A visually similar site from the mountain top was analysed using the Tracer, corresponding to site 1 examined by MOLAB. Principal peaks for zinc, lead and cobalt were detected for site 5, corresponding to the blue and white wet-in-wet mixture of pigments analysed by SEM/EDX. This site is one of very few areas examined by MOLAB that did not record a peak for barium corresponding to the ground layer, perhaps because the paint over the ground was thicker in this area. Minor peaks of titanium, manganese, iron suggest the presence of an earth pigment. Also copper and arsenic were recorded, suggesting the possible presence of emerald green amongst the pigment mixture in this site. Elements indicating the presence of French ultramarine were beyond the limits of detection of the MOLAB equipment.

Site	Site description	Elements MOLAB XRF	Elements Tracer
1	Blue mountain	(Ca) (Ba) (Mn) (Fe) Co Cu <u>Zn</u> <u>Pb</u> As (Hg?)	<u>S</u> Ca (Fe) <u>Co</u> <u>Cu</u> <u>Zn</u> <u>As</u> <u>Pb</u>
2	Blue mountain 2	(Ca) (Ba) (Mn) (Fe) Co Cu <u>Zn</u> <u>Pb</u> (As) (Hg?)	
3	Blue mountain top	(Ca) (Ti/Ba) Cr (Fe) <u>Co</u> <u>Cu</u> <u>Zn</u> <u>Pb</u> As	
4	Dark blue mountain	(Ca) (Ba) Cr (Fe) Co <u>Cu</u> <u>Zn</u> <u>Pb</u> As	
5	Blue sky	(Ca) (Ti) (Mn) (Fe) Co (Cu) <u>Zn</u> <u>Pb</u> (As)	<u>S</u> Ca (Fe) <u>Co</u> <u>Cu</u> <u>Zn</u> <u>As</u> <u>Pb</u>
6	Green leaf right edge	(Ca) (Ba) (Mn) (Fe) Co <u>Cu</u> (Zn) <u>Pb</u> (As)	(S) Cr <u>Cu</u> <u>Zn</u> <u>As</u> <u>Pb</u>
7	Cloud over green leaf	(Ca) (Fe) (Co) Cu Zn <u>Pb</u> As	
8	Dark green leaf	(K) (Ca) (Ba) <u>Cr</u> Fe Cu Zn <u>Pb</u> (As)	
9	Dark green leaf	(K) (Ca) (Ba) Cr Fe (Co) Cu <u>Zn</u> <u>Pb</u> As	
10	Light green leaf	(K) (Ca) (Ba) Cr Fe (Co) Cu <u>Zn</u> <u>Pb</u> As	
11	Bright blue	(K) (Ca) (Ti/Ba) (Fe) Co, (Cu) <u>Zn</u> <u>Pb</u> (As)	
12	Black	(K) (Ca) (Ba) (Cr) Fe (Co) <u>Cu</u> <u>Zn</u> <u>Pb</u> As	
13	Yellow wash above leaf	(K) (Ca) (Ba) Cr Fe Co (Cu?) <u>Zn</u> <u>Pb</u>	
14	Yellowish green	(Ca) (Ba) Cr Fe Co Cu, Zn Pb As	S (Ca) Fe Zn (Hg?) Pb
15	Red part of tree	(K) Ca (Ti/Ba?) (Cr) Fe (Cu?) <u>Zn</u> <u>Hg</u> <u>Pb</u>	S Ca (Fe) <u>Zn</u> <u>Hg</u>
16	Dark blue of tree	(K) (Ca) (Ti/Ba?) (Cr) Fe Co Cu <u>Zn</u> <u>Pb</u> (As)	
17	Dark yellow wash	(K) Ca (Ba) Cr, Fe Cu, <u>Zn</u> (Hg), <u>Pb</u> (As)	
18	Green wash	(K) Ca (Ba) Cr Fe Co <u>Cu</u> <u>Zn</u> <u>Pb</u> As	
19	Violet of tree	(K) (Ca) (Ba) (Cr) Fe Co Cu <u>Zn</u> <u>Hg</u> <u>Pb</u> (As)	
20	Brown	(K) Ca (Ba) (Cr) Fe Cu Zn <u>Pb</u> (As)	
21	Brown/yellow	Ca (Ba) (Cr) Fe (Cu) Zn (Hg) <u>Pb</u> (As)	
22	Light yellow of hill	Ca (Ti/Ba) (Cr) Fe Cu <u>Zn</u> <u>Pb</u> <u>As</u>	
23	Reddish yellow of hill	Ca (Ba) (Cr) Fe (Cu) <u>Zn</u> <u>Hg</u> <u>Pb</u> (As)	
24	Yellow of house	(Ca) (Cr) Fe (Cu) Zn (Hg?) <u>Pb</u> (As)	(S) Ca Cr Fe <u>Cu</u> <u>Zn</u> <u>As</u> <u>Pb</u>
25	Dark green	(Ca) (Ba) (Cr) (Fe) (Co) <u>Cu</u> <u>Zn</u> <u>Pb</u> <u>As</u>	
26	White of road	(Ca) (Ba) (Cr?) (Fe) (Cu) <u>Zn</u> <u>Pb</u> (As)	
27	Dark green	(Ca) (Ba) <u>Cr</u> (Fe) (Co) <u>Cu</u> (Zn) <u>Pb</u> <u>As</u>	
28	Light green	(Ca) (Ba) Cr (Fe) (Co) <u>Cu</u> <u>Zn</u> <u>Pb</u> <u>As</u>	S (Ca) (Cr) <u>Cu</u> <u>As</u> <u>Pb</u>
29	Light yellow	(Ca) (Cr) Fe <u>Zn</u> (Hg) <u>Pb</u>	
30	Orange area near 29	(Ca) (Cr) Fe <u>Zn</u> (Hg) <u>Pb</u>	
31	Blue underpaint	(Ca) Ba Fe (Zn) <u>Pb</u>	
32	Signature	(K) (Ca) (Ba) Fe (Zn) <u>Pb</u>	<u>S</u> (Ca) (Fe) <u>Pb</u>
33	Signature	(K) (Ca) (Ba) Fe (Zn) <u>Pb</u> (Sn?)	<u>S</u> Ti? Zn Pb
34	Loss in ground	(Ca) Ti (Fe) <u>Zn</u> <u>Pb</u>	
35	Reverse of canvas	(Cl) (K) Ca Fe Zn <u>Pb</u>	
36	Reverse of canvas	(Cl) (K) Ca Fe Zn Pb	

Table 2. XRF analysis results of The Montagne Sainte-Victoire using MOLAB equipment.

Site location see Fig 2. Acquisition time 120 sec.

The visually similar site of the mountaintop gave a well resolved spectrum using the Tracer instrument set to 15kV, 15 $\mu$ A with the sensor under vacuum. Principal peaks were detected for lead, arsenic, zinc, copper, cobalt, and sulphur, with smaller peaks for iron and titanium. This suggests the presence of cobalt blue with emerald green, either as a mixture or in overlying layers, as well as the white pigment mixture detected in EDX. French ultramarine was not detected by XRF, despite using the optimum settings for the detection of aluminium; but the pigment may not have been present in the specific passage of paint analysed. The MOLAB instrument recorded similar principal peaks, with additional minor peaks for calcium, barium and manganese, and no sulphur peak.

Green paint passages varying from deep blue green to bright yellow green were analysed using the MOLAB instrument, whilst two sites were examined with the Tracer. Copper and arsenic peaks corresponding to emerald green were consistently detected, together with chrome in sites 8, 9, 10, 27 and 28 and particularly in the bright yellow green of site 14, indicating the addition of chrome yellow to the paint mixture. A peak for cobalt was detected in site 6 where the leaves of the trees are thinly painted over the sky. The Tracer recorded the presence of emerald green in both green passages analysed, with small peaks for chrome.

The bright yellow used in the houses on the left hand side of the painting (site 24 in the MOLAB study, and the yellow rooftop in the Tracer study) was analysed using both techniques, and peaks for iron, zinc and lead were detected. Set to 40kV, 1.5 $\mu$ A, the Tracer detected additional large peaks for copper and arsenic, suggesting the presence of emerald green, and using the instrument set to 15kV, 15 $\mu$ A with the sensor under vacuum, further small peaks for chrome and calcium were detected. The MOLAB spectrum registered copper, arsenic, chrome and calcium as minor peaks, suggesting a slightly differing paint mixture in the area examined. It is not clear from either spectrum whether chrome yellow (perhaps zinc or lead chromate) is the principal yellow pigment in this area, and it would rather appear that the chrome is associated with the emerald green, as found elsewhere on the painting. The use of yellow ochre, indicated by the iron peak, could be hypothesised. More firm conclusions on the presence of certain pigments or mixtures of pigments and/or inorganic additives might be made applying Principal Component Analysis on the present data (Rosi et al. 2008).

Both techniques recorded mercury, indicating vermilion was the red pigment used in the bark of the foreground tree. The dark blue paint used for Cézanne's signature was examined by both XRF methods and neither could conclusively identify the blue pigment, owing to the poor detection of light elements which might identify ultramarine. A minor peak for iron with a larger peak for lead was recorded by the Tracer, whilst principal peaks for iron and lead alongside minor peaks for potassium, calcium, barium and zinc comprised the MOLAB spectrum. The use of Prussian blue mixed with lead white was confirmed by FTIR analysis conducted by MOLAB, and red lake was identified using the light microscope.

## **DISCUSSION AND CONCLUSIONS**

The use of XRF techniques for the study of paintings by Paul Cézanne was essential in the characterisation of his palette for works in excellent condition with little opportunity for paint sampling. The non-invasive methods of analysis meant that sites for examination were only limited by the time available, allowing comprehensive characterisation of paint passages.

The work on paper *Apples, Bottles and Chair Back* proved well suited to the XRF technique, where watercolour is applied in relatively thick and concentrated dashes of colour, rather than

as thin washes. The paint passages appear to be applied in single layers, and with little mixing of colours, allowing for more straightforward interpretation of elemental data gathered using both instruments.

The interpretation of data was critically affected by the poor spatial resolution of XRF. Where possible, the comparison of spectra obtained from unpainted ground or paper with that obtained in painted areas provided clarification, but meant that the presence of certain elements could not be definitively assigned to the paint or underlying layers. The characterisation of indigo blue used in the watercolour, distinguishable from Prussian blue (used in the oil painting) was achieved by supplementary FTIR analysis conducted by MOLAB that is beyond the scope of this paper, but the necessity for complimentary analytical methods for characterisation of pigments is highlighted.

Quantitative assessment of peak heights using the Tracer instrument was affected by the capture conditions of the spectra, which were weighted towards different regions of the periodic table. Ideally, each site should be analysed using all three conditions to give a more complete view. Lack of experience on the part of the operator limited interpretation for this study, and whilst the accompanying software is very accessible, issues of detection and peak overlap remain. As a result the interpretations given in this paper may not entirely reflect the capabilities of the instrument. Equally, the conditions selected for analysis using the MOLAB XRF could have been optimised to favour the acquisition of selected elements. As these parameters were not varied it was not possible to make a valid comparison between the different XRF instruments. While both instruments were easy to use, the relative ease of the lightweight Bruker instrument proved advantageous offset by the necessity to place the instrument in direct contact with the surface of the work of art to obtain the best results.

Comparison of the spatially resolved elemental analysis of the cross-section taken from *Montagne Sainte-Victoire* suggests that caution should be exercised in the interpretation of XRF data gathered from paint consisting of complex pigment mixtures. One example illustrated in the present study is the interpretation of the presence of zinc that could be found as zinc oxide pigment, zinc oxide added to lead white pigment, alternatively zinc may be associated with yellow or orange chromate (or cadmium) pigments, or present as lithopone extender (barium sulphate with zinc sulphide). The use of extenders and other inorganic additions to paint preparations is a particularly important consideration in works from this period (Carlyle 2001). Statistical treatment of the data falls outside the scope of this paper but would be helpful in resolving these issues, as shown by the MOLAB team in a separate paper (Rosi 2008). Characterisation of French ultramarine using XRF is problematic, particularly where compounds of other pigments containing Al, Si and S are present. This highlights the difficulty in interpreting data from blue paint mixtures. Whilst the MOLAB instrument could not detect any of the elements required to identify ultramarine, using the Tracer it was possible to acquire small peaks registering the presence of the characteristic elements from the pigment only where it was present in relatively high concentration. This has important implications for the detection of aluminium, at the limit of its sensitivity.

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