# Submission to the Parliamentary Inquiry into Australia's Indigenous Visual Arts Sector

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**OCTOBER 2006**

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Senate Environment, Communications, Information Technology and the Arts Committee
Department of the Senate
PO Box 6100
Parliament House
Canberra ACT 2600
Australia

*November 4th 2006*

Dear Dr Holland,

**RE: INQUIRY INTO INDIGENOUS ARTS SECTOR**

As indicated by several recent media reports, Indigenous art fraud in Australia is on the rise. This negatively impacts on consumer confidence in purchasing these works of art, ultimately affecting the Indigenous artists themselves, their culture and their heritage.

Over the past four years, members of our research group have undertaken research projects into the development of methodologies which enable the identification and authentication of artwork. This research produced promising results which has enabled the establishment of the current and ongoing research project in conjunction with the Jirrawun and Warmun arts communities in Western Australia and with the support of both the Art Galley of Western Australia and the ANKAAA. Although the research is ongoing we have obtained results that indicate that the established chemical methodologies are able to reliably identify and therefore, authenticate aboriginal artwork. In addition, chemical technologies have been investigated which may enable the artist to protect their works against fraudulent manufacture. We are also hopeful that this technology will refine the authentication process making it not only more reliable or robust but also simpler.

The primary objective of our research is to develop a technology and methodology which can assist in the protection of the aboriginal art culture and heritage for future generations. The ability to authenticate these artworks will also assist in the maintaining of the integrity in the trade of aboriginal artwork. The current research provides the foundation necessary to achieve this objective. However, financial support is essential to ensure the technology is developed and tested to a point where it can be implemented and widely used.

Please find attached the submission to the Senate Environment, Communications, Information Technology and the Arts Committee, detailing both the research undertaken in the past as well as that currently being undertaken at the University of Western Australia.

Sincerely,

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# INQUIRY INTO AUSTRALIA'S INDIGENOUS VISUAL ARTS AND CRAFTS SECTOR

# FORENSIC CHEMISTRY AND CRIMINALISTICS

## Protection of Cultural Heritage: Forensic Science and the Authentication of Australian Artwork †

Rachel L Green and R John Watling

† Presented at the 2006 Winter Conference on Plasma Spectrochemistry in Tucson, AZ on January 8-14, 2006 and the Australian and New Zealand Forensic Science Society 18th International Symposium on the Forensic Sciences held in Fremantle, Perth on April 2-7, 2006. The research discussed below has been accepted for publication in the Journal of Forensic Sciences.

## ACKNOWLEDGEMENTS

The authors wish to thank Rio Tinto – Argyle Diamonds for their financial contributions to ensure these research goals are achieved and implemented. Thanks to the staff at the Art Gallery of Western Australia, in particular Ms Natalie Hewitt, Ms Vanessa Roth and Ms Clotilde Bullen for their time as well as the ochre and artwork samples provided for this research. Furthermore, the authors wish to thank Ms Stephanie Hawkins at the Association of Northern, Kimberley and Arnhem Aboriginal Artists Inc. and the Indigenous communities throughout Western Australia and the Northern Territory who assisted with sample collection and background information.

## INTRODUCTION

In November 2005, Senator Amanda Vanstone declared that Aboriginal art was "Australia's greatest cultural gift to the world". Aboriginal paintings represent some of the worlds oldest art yet their tradition, modified through generations of indigenous culture, is at present one of the most fascinating and popular modern investments in the art market. Investors are accrediting this attention to the cultural, historical and transient qualities that make the artwork unique as well as the professionalism of its execution and the intense and complex beliefs it represents. The explosion of interest in Indigenous artists and their artwork has created an abundance of opportunity for the Aboriginal people of our country. However this interest, generated at both a domestic and international level, is a double-edged sword. Greater awareness and appreciation of both the quality and cultural significance of these artworks means that the price investors are willing to pay for genuine works has increased substantially. As a result, there has been an equivalent growth in the 'Black Market' for these works and in the production of fraudulent copies. Fraudulent artworks are not only demeaning to the implicated artist, but as these tales are passed from generation to generation, forged works of art represent a definite insult to indigenous culture. For that reason, protection of the integrity and authenticity of the artwork is vital as it is not only an issue of individual artists being defrauded, but an issue of Australia's cultural heritage being undermined.

**Figure 1: Carol Johnson -** *Mistake Creek Massacre*
*Courtesy of Warmun Art Centre (2006)*

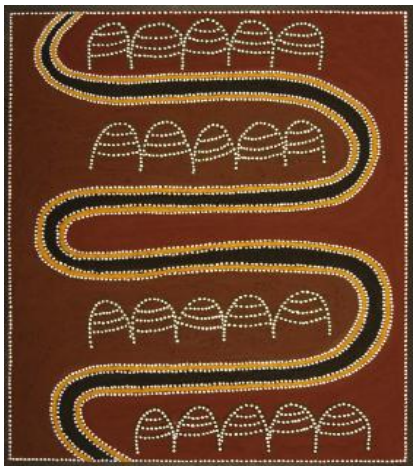

**Figure 2: Christopher Churchill -** *Ord Road (Jarlarloo)*
*Courtesy of Warmun Art Centre (2006)*

Art forgery has existed as long as there has been valuable and admired art. Most artistic techniques or styles can be copied by a skilled individual and are often difficult to distinguish from the original. Western Australia alone exports some $500 million dollars worth of Indigenous art per year. As a substantial part of the art industry, if the authenticity of this artwork is questioned internationally and no protocols are in place at source to identify and eliminate fraud, the economies at both a state and national level will suffer the consequences seeing that the international community lacks confidence in Australian Aboriginal art.

Artwork authentication is a subjective process made even more difficult by technological developments, which assist the forger in creating quality copies. The processes utilized for distinction between pieces are entirely non-scientific and are conducted by art specialists, whom rely heavily upon visual examination; assessing painting styles, textures and artistic signatures in order to make a judgment as to the authenticity of a painting. This illustrates the desperate need for the development of authentication techniques which are less subjective than those currently practiced. Subsequently, a variety of scientific tools are becoming available to curators and art historians, exploring not the style of the painting itself, but rather the chemistry of artwork media. Given monetary transactions between purchasers and galleries or art centres are at a record high, it remains imperative that a reliable and valid scientific method for provenancing traditional indigenous artistic material. Once established, this method can, if necessary, be used to assist in authentication of artworks. This issue was raised in 2001 with the NSW Legislative Committee. Michael Egan, the former Minister for Arts, was asked to detail actions the government has taken to ensure that copying or forgery of indigenous art is outlawed, given the negative impact this activity has on communities whose income is solely based around the sale of art. At that time and still today, these questions have not been answered. Indigenous art fraud is rife and there are no substantial authentication protocols in place to inhibit both the production and sale of these works.

**Figure 3:** Mabel Juli paints at Warmun Art Centre, WA (2006)

Paint and canvas has given the Aboriginal people a chance to record Dreamtime stories in a permanent form. Traditional artists use materials sourced from an immediate area of particular cultural or ancestral significance to them, thus provenancing these materials should theoretically enable the scientist and art historian to relate the artwork back to the area of origin. The vast majority of traditional paintings within gallery collections were created using natural pigments, with ochre being the most common inorganic pigment used. Modern artists favour bulk synthetic materials such as acrylic, oil and watercolour media due to the greater colour and texture choices. However, these materials are prepared in mass and thus the chemical composition does not differ greatly. This means that there is a decreased ability to establish provenance of artwork created at two different art centres but by artists using the same brand of synthetic paint, based upon pigment analysis alone. Consequently, current research initiatives focus on the analysis of acrylic paints, binders, fixatives and the supporting media (canvas) in an effort to establish suitable protocol for provenancing and authenticating both modern and traditional indigenous art works.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was utilized for trace elemental analysis and provenance establishment of ochre samples. Ochres consist primarily of the oxides and hydrated oxides of iron (hematite and goethite), silicon (quartz), aluminium (clay) and manganese and are commonly observed in traditional indigenous art or early human rock art. The resulting elemental distribution pattern or 'fingerprint' of a sample reflects the source or origin of that sample. Therefore, samples from the same source are co-provenanced and have a correlated fingerprint. Using this qualitative method, we are able to distinguish samples from one another. This research was used to develop a robust scientific protocol which facilitates definitive and accurate determination of provenance of Australian ochres and the artworks created using them. Ochre of known provenance was analysed using LA-ICP-MS and data processing achieved using a variety of statistical and chemometrical procedures including ternary plots, principal component analysis, chondrite normalisation and in-house search-match procedures. Results were compared and plotted, to illustrate population separation and identification of samples based on their chemistry. These differences were identified, both between regions and within a single region, to ascribe provenance to artworks produced using the individual ochres. Furthermore, construction of databases for both synthetic and naturally sourced artists' media will provide sufficient resource for comparison of questioned artworks, thus assisting investigators with their fraud enquiries.

There exist a myriad of applications for this technology; from determining ochre provenance to manufacturers of acrylic, oil and watercolour paints to detecting fraudulent ceramic pieces. Aside from application within the art industry, this technology has been utilized for criminal investigation purposes through the analysis of projectiles (bullets), glass evidence, gold, diamonds and explosive residue. As with all analytical methods, laser ablation has limitations including the lack of available certified reference material. That means that at this stage, analyses are only semi-quantitative. Full quantitative analysis is a major objective, but this requires further research to determine the most suitable and accurate way to undertake this.

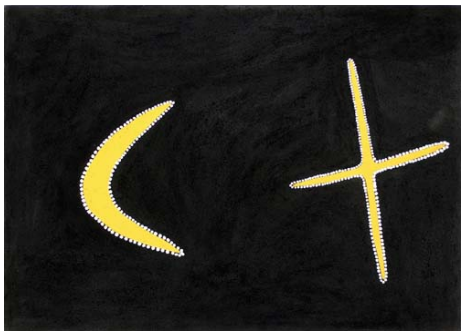

**Figure 4: Mabel Juli -** *Ngarrangkarni Moon Dreaming*
*Courtesy of Warmun Art (2006)*

Our current laser system, a New Wave 213nm laser coupled to an Agilent 7500CS series octopole inductively coupled plasma mass spectrometer (Figure 5) is being used for all future experiments. The system has the capability to analyse samples only 10 microns in size (1/100 of a millimetre), so even though laser ablation is a destructive technique, the level of destruction is microscopic. Samples can be obtained from under the frame of a painting or from the reverse of a canvas and thus the value of an artwork is preserved. Presently, a scraping is required from the artwork, as the entire painting does not fit within the sample cell. A speck of paint 50 microns in size is sufficient for trace elemental analysis and by taking the sample from under the frame, we can ensure that airborne contamination and damage to the artwork, will not be issues. However, upon the outcomes of research conducted by Ms Kari Smith, we should have a portable laser system operating, which will allow us to visit galleries and sample in-situ.

**Figure 5:** The New Wave 213nm laser system and Agilent ICP-MS instrument at UWA (2006)

While traditional techniques have their use, a significant number of instances occur where definitive provenance establishment cannot be proved and additional corroborative techniques are needed. At this stage quantitation of the sample material is not possible due to a number of understood factors that, for some matrices, present an insurmountable problem. However, this is not necessarily true for paints, fixatives and binders. Consequently, research was conducted in order to develop the first methods for the specific quantification of the chemical composition of these materials and to develop a series of robust protocols that may be used to relate the chemical composition of both natural and manufactured pigments to individual artists and art cooperatives thus assisting in the validation and authentication of indigenous works of art. Additionally, a database was developed to be used to assist in the provenance establishment of recovered material. However qualitative analysis provides us with sufficient information to determine whether or not two samples have a common source. This type of analyses is depicted in Figure 6, where two different ochre samples have been analysed and the data plotted. The isotopic distribution patterns ('fingerprints') of the samples display some quite obvious difference, which allows us to state the two samples do not originate form the same source.

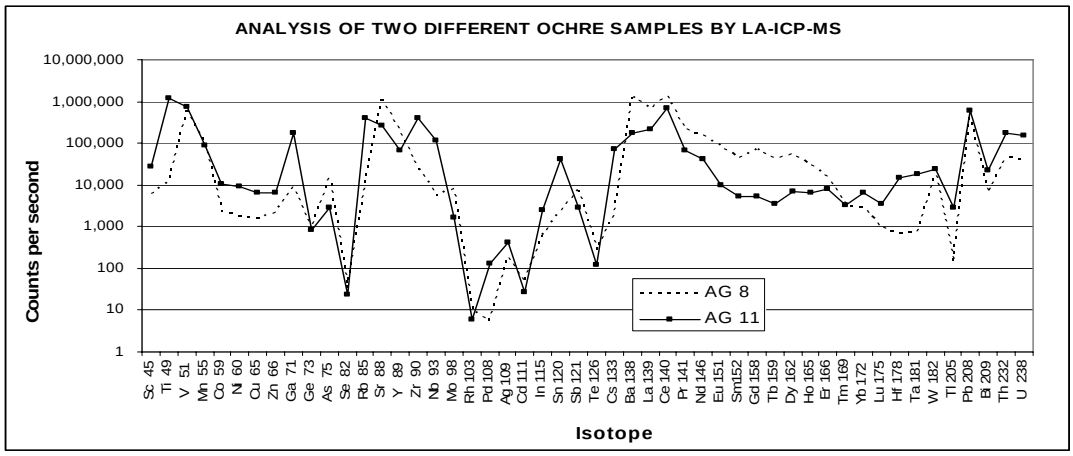


**Figure 6**: Example of an elemental distribution plot of two different ochres, AG8 and AG11. Differences are easily observable.

## THE RESEARCH

Provenancing artistic media using laser ablation for authenticating artwork has never been undertaken before, making this research the first of its kind worldwide. Although connected primarily to Australia artworks, in particular Indigenous artworks, once protocols have been developed fully, these may be applied to all types of artworks internationally. Ochre samples collected from across Australia and internationally have been analysed and compiled into a database. In addition to this, several hundred acrylic, oil and watercolour paint samples donated or purchased from various manufacturers are being analysed by laser ablation and a database compiled.

Further organic and spectrometric analysis will be undertaken in the coming months to support the findings encountered using the laser technology and to determine whether provenance of the materials can be more reliably established. Organic

analysis as well as mineral grain identification will aid this. As companies manipulate methods of production, the trace elemental signatures may alter over time. However, by building a database and monitoring these changes, this will not become an issue

Additionally, current technological developments include chemically altering the artistic media to assist provenance establishment of the material. This involves chemically 'spiking' the paint, support matrices or the ink used to sign the artwork with a carefully prepared cocktail of elements. The elemental combination and the quantities will be specifically related to a particular artist or time period. By then analysing the paints or support matrices, we will be able to determine the artist, place of creation and date the painting was encoded, thus ensuring unambiguous scientific provenance of valuable artworks.

This technology is to be applied to artworks created by the Jirrawun arts community in Kununurra at the request of the centre's director, Mr Tony Oliver. Mr Oliver is a great supporter of this research and has provided us access at an arts exhibition taking place in Sydney through December and January of 2006-07. During this exhibition, we will chemically encode the paintings of Mr Paddy Bedford, a renowned and respected indigenous artist to ensure Mr Bedford's works are protected from attempts at forgery.

## SUMMARY OF RESULTS

- Ochre samples sourced from different regions within Australia had unique and distinguishable trace metal signatures. The reproducible overlaying of trace elemental signatures for each replicate suggests that laser ablation ICP-MS has excellent application for the analysis and provenance establishment of ochre samples.
- Analytical reproducibility is proof that only a single sample of ochre from a specific site is required to obtain accurate and representative trace elemental concentrations for ochres from that site.
- A single fragment of ochre sampled from an original artwork is sufficiently homogenous for data obtained from its analysis to be used legitimately to establish geographical origin.
- The artwork samples could be related back to ochre samples of the same mineralogy and geological origin.
- Sample powdering procedure had no effect on the trace elemental composition, with the exception of an increased detection of cobalt and tungsten. This increase in specific elemental concentrations is to be expected as incorporation of abraded material from the ring mill results in contamination by these metals. However, the increased levels of these metals do not cause problems with the provenance establishment mathematical protocols and do not lead to false provenance identification, as tungsten and cobalt are not used for provenance establishment purposes.
- Additives, including PVA glue and local Warmun water used to produce the traditional ochre paint, were analysed. The majority of elements were detected at levels approaching the instrumental detection limits. The additives were found to not significantly contribute to the elemental fingerprint of the paint. Therefore, if an ochre sample from an artwork is analysed and the data compared with the data for the original ochre, the inter element association patterns for both will essentially be identical.
- Using various statistical manipulations, all ochre samples analysed so far were discriminated from each other. Furthermore, discrimination within a single region allowed ochre samples collected from within 50km of each other, to be chemically separated. Therefore, once a database is established, an unknown sample may be analysed and determined to have originated from within a 2500km$^2$ area of land. This relates to an extremely specific region when the size of the country is taken into account.
- Further research was conducted to test the validity of the study procedures for provenancing fraudulent artwork. A sample of artwork was analysed together with ochres from various regions across northern Australia. It follows that the materials used on these artworks are of the same origin and thus may be linked through their inter-elemental ratios determined using this technique. A search/match screening protocol was used to determine how comparable the ochres from the Tiwi region were with the artwork sample. From these analyses, the elemental distribution patterns of both the Tiwi Island ochre samples and samples from the artworks were found to match. This proves that they originated from the same source. As such, the utilization of LA-ICP-MS for establishing provenance of artworks through ochre analysis has been established.

## CONCLUSIONS

A database of ochres has also been initiated. Although more samples from more regions around Australia are required before it can be put to practical use, ultimately it is hoped that by using this database, ochres may be related back to a particular geographical origin within Australia and artworks can be unambiguously associated with a particular artist. Given the protocol for establishing provenance of ochre samples and in turn artwork samples has been established, the potential to establish a comprehensive database exists. This database, centred on the ochres' specific trace elemental distribution

pattern, would facilitate retrospective searching and provenance establishment of existing artworks. The specific 'fingerprint' of the ochre would be stored electronically and compared with similar 'fingerprints' from spatially associated equivalents to establish regional 'fingerprints'.

In this way, identification of regional variations in natural pigments is possible, which can be related back generically to regional art centres. This database could then be used to determine if the ochre on a particular artwork came from the area used by that artist. A specific fingerprint could then be used as evidence of the ochre's identity and origin and its potential association with a regional school of art and artist. Once established, the identity of the ochre may assist the legal process by providing supporting evidence in fraud investigation.

## FINANCIAL SUPPORT

- Rio Tinto - Argyle Diamonds PhD scholarship: AU$30,000 pa for 3 year duration of research. This encompasses an AU$9000 maintenance fund, utilised for travel and research expense purposes.
- 2006 UWA University Graduate Research Candidate Travel Award - AU$1520 to cover the costs of travel to the international conference.
- 2006 Winter Plasma Spectrochemistry Conference Travel Award – US$200 prize (donated by Gary Hieftje and Associates) Conference registration and dinner were also covered in the award.
- Australian and New Zealand Society for Mass Spectrometry Travel Award – AU$400 for travel costs incurred as a result of attending Winter Plasma Spectrochemistry Conference.

## EXPERT INVOLVEMENT

LOCAL

- Dr John Stanton - Curator/Director, Berndt Museum of Anthropology (Vice-Chancellery) at UWA

*Dr Stanton has provided access to the extensive Indigenous art collection at the museum. He is also a co-supervisor for this research.*

- Ms Clotilde Bullen - Indigenous Art Curator at the Art Gallery of Western Australia

*Ms Bullen has been invaluable to this project. She has provided access to the Art Gallery of Western Australia's artwork collection as well as knowledge in the area of Indigenous artists and assistance with interpreting paintings. Ms Bullen is also an external supervisor for this research.*

INTERNATIONAL

- Dr Tom Learner - Conservation Department, Tate Gallery, London, United Kingdom

*Dr Learner has vast experience with research and analysis of modern artistic media.*

- Professor J. David Robertson - MURR Associate Director of Research and Education, University of Missouri

*Professor Robertson has extensive experience with provenancing natural materials including ochres, commonly found on African and Native American artefacts.*

- Professor Robin Clark - Christopher Ingold Laboratories at University College London

*Professor Clark has extensive experience in the analysis and composition of artistic media and inorganic chemistry in general*

- Professor Jon Erlandson - Forensic Anthropologist, University of Oregon

*Professor Erlandson has extensive experience in anthropology and in particular the protection of Indian American culture through ochre analysis.*

- Ms Stephanie Guigou – Manager, Société des Ocres de France

*As the last operating ochre company in Europe, Ms Guigou has been assisting us with samples of European ochre.*

- Mr Jody Bretnall – Founder of Guerra Paints and Pigments, New York City USA

In addition to experts in the field, there are a number of companies and art centres worldwide that have assisted greatly with information and samples. These include *Lascaux Colours* (Ms Barbara Diethelm and Ms Sandy Schroeder), *Sinopia Pigments, Golden Paints* (Mr Mark Golden), *Chroma Australia* (Mr Wayne Gates – CEO) , *Lukas* (Ms Ute Hallebach), *Schmincke, Royal Talens* (Mr Matthijs de Keijzer and Mr Bert Klein Ovink*), Genesis Art Supplies* (Mr Rex Cooper), *Matisse Derivan* (Mr Steven Patterson), *Liquitex* (Mr Scott Present), *LeFranc & Bourgeois* (Mr Pascal Roy), *Sennelier Pigments* (Mr Dominique Sennelier) and *Superfine Colours South Africa* (Mr Kelvin Irvine).

Most importantly, is the cooperation of the Indigenous artists and people throughout Australia. Various communities in northern Western Australia and the Northern Territory have been of great assistance. In particular, the Jirrawun, Warmun and Waringarri art communities have provided ochre samples and support for this project. Further assistance has been maintained through the support of the South Australian, New South Wales, and Queensland state museums and art galleries.

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# PAST AND CURRENT FORENSIC RESEARCH

**MS KRISTIN HORTON**

# *Provenance establishment of pallet paints with respect to the identification of forged art.*

**2003**

## PROJECT OBJECTIVES

The main objectives of this research were to:

- prepare and analyse a number of acrylic, oil and watercolour paints to determine their trace elemental composition.
- study the effect of fire on the element profiles of artist's paints by using various ashing techniques. The findings have a potential application in the fields of arson investigation or insurance fraud. If it is claimed that an expensive painting was destroyed in a fire, then analysis of the element profile of the ash was able to validate the paintings authenticity.
- determine whether is it possible to samples historical artistic media and trace the development and modification of the painting material of a particular artist through time thus enabling time-based forgeries to be identified. For this study, the works of Australian artist, Kathleen O'Connor covering the period 1911-1962 were used.
- use Raman Spectroscopy as a non destructive and complimentary technique to ICP-MS for the provenance of modern artist's pigments.

## RESULTS

The data obtained using ICP-MS was interpreted, where appropriate, based on the method outlined in 'Metals in Antiquity' (Watling et al, 1999). The reproducibility of the data was quite high, meaning the data obtained was reliable.
As sampling of artworks does not always permit the collection of a clean paint fragment, it is necessary to determine what contribution the support that the fragment is adhered to, has on the elemental profile of the paint sample. Investigation of three support matrices; canvas, watercolour paper and Masonite, found that;

- Canvas – analysis of the blank canvas showed that the canvas contains much higher levels of $^{65}Cu$, $^{73}Ge$, $^{75}As$, $^{82}Se$, $^{95}Mo$, $^{111}Cd$ and $^{121}Sb$ than the paint sample contained. However, the trends between the element profiles are exceptionally close suggesting the two samples are from the same sub-population and indicating that any elemental contribution from the canvas is insignificant
- Paper - The element profiles were well correlated, suggesting that the paper support does not affect the element composition of the paint samples as much as the canvas. The paint, when analysed on the watercolour paper, contains proportionally more of each element. This is more likely due to slight differences in ablation efficiency than contribution from the support.
- Masonite - The element profiles had a high degree of correlation signifying that there is minimal incorporation of the support matrix elements into the fingerprint and that under these ablation conditions, the Masonite support does not affect the element composition of the paint samples as much as canvas.

### Arson Investigation

All paint samples were ashed in a furnace, under an oxygen-poor environment. This simulation of an arson incident was conducted to determine if it was possible to provenance a painting despite the work being burnt. Comparison of the element profiles obtained from different burning conditions yielded fairly reproducible results. This suggests that variability between the concentrations of elements is proportional and differentiation between samples should be based on crossing over of trend lines in the element profile.

Each ashed artist's paint was compared to the database of reference artists' paints to determine if the element profiles could be matched. Close similarities in general trends were observed between the element profiles however the ashed samples had a tighter correlation. As such the ability to provenance ashed paint to the unmodified reference sample is limited. An additional database of the element profiles of ashed artist's paints is therefore recommended as a more accurate comparison base for the reasons discussed previously.

The experiment was broadened to include analysis of ashed paints on the support. The elemental fingerprints were found to match, supporting the theory that the support matrix does not significantly affect the elemental profile of the point. However, ashing paints in a furnace was an artificial environment. Therefore, in order to better understand the effect of fire on paints, paint was applied to canvas and paper and the samples cut into strips and sandwiched between wooden beams. The wooden frame was set alight and allowed to burn. When the frame was pulled apart it was noticed that the majority of the sample had been protected, with only the outer edges charring. Sampling was undertaken from the charred and unmodified sections and analysed using both solution and LA-ICP-MS. Both the ashed (outer) and protected (inner) paint samples had an equivalent trace element profile suggesting that, after an arson incident, it would still be possible to provenance recovered paint.

### Analysis of Artwork Pigments from Kathleen O'Connor Paintings

A number of samples were collected from several paintings by Western Australian artist, Kathleen O'Connor covering the period of 1911-1962 and analysed using LA-ICP-MS. The exact dates of commission for these paintings were unknown, but it was possible that the same painting materials would have been used for the paintings and this would be reflected in the element profiles of the samples taken. The resulting element profiles used to trace the changes in the painting material

through time. ‘Still Life with Fish’ (commission date unknown) was determined to be painted around the same time as ‘Portrait of Sir Russell Dumas’ (1962). The use of this technology for chronologically dating paintings can therefore be confirmed.

## CONCLUSIONS

- A number of databases were developed containing the element composition of artists’ paint applied to canvas, watercolour paper and Masonite. Any contribution of elements form the support was minimal. The elements that varied the most between the profiles were consistent with those elements present in higher levels in the support. These elements were removed from the element profile and the residual profiles compared, resulting in a higher degree of similarity. However, further research is required to develop databases allowing more accurate comparison of these materials.
- The effect of ashing on the element composition of artist’s paints was investigated and proved that it is possible to provenance recovered paint samples from an arson scene. However, a specific database of the element profiles of the ashed paints is needed for a comparison base.
- Paint samples extracted directly from paintings allowed a historical timeline of commission dates for paintings to be determined. By matching the paints from the different artwork pallets, the paintings can be chronologically ordered. Therefore, using this technology is remains possible to take historical material and trace the development and modification of the painting material of an artist through time.

**MS HEIDI WOODS**

# *The application of Laser Ablation Inductively Coupled Plasma Mass Spectrometry in the provenance establishment of arson debris with particular regard to artistic media*

**2005**

## PROJECT OBJECTIVES

The main objectives of this research were to:

- confirm and further establish the feasibility of a trace element fingerprinting technique, using laser ablation ICP-MS, for a variety of artist grade paints. Horton's work was continued to include forty five paints; based on five colours, three paint types and a variety of manufacturers.
- establish differentiation between samples which are not derived from a similar background and to correctly identify those which are derived from the same source. Essentially, to differentiate between colour, make and paint type via the identification of specific elemental markers and patterns for specific sample categories.
- identify the level of retention of original trace elements within a given paint sample, following exposure to conditions of arson conducted at 200, 400, 600 and 900ºC throughout time increments up to 4 days.
- determine whether results for a single sample remain comparable before and after the heating process.
- identify the impact the support media has upon trace element fingerprinting.
- determine whether a given elemental fingerprint remains identifiable when combined with that of support media and, if this is not the case, the feasibility of using statistical methods for its correction.
- establish a trace element profile database for a variety of paints using LA-ICP-MS, which may potentially allow for the identification of unknown samples, distinguishing between colour, manufacturer and paint type, including heat affected samples.

## RESULTS

Analysis of the original samples indicated not only that each sample was characterised by a unique trace element profile, but that this profile was reproducible under equivalent conditions of analysis. Attempts to classify the entire data set using statistical methods were unsuccessful, indicating that the given profile of a sample is affected by more than one independent variable. These factors were colour, manufacturer and media type. Each of these factors were analysed for separately and the result concluded there was distinction between different colours, manufacturer and media types. As such an unknown sample heated or not, could be classified by colour, manufacturer and media type when compared to an appropriate and comprehensive database of artists' materials.

Arson situations were tested. The results of this study are significant in that they indicate that there is not a requirement for the temperature or heating interval of a fire to be known in order to potentially trace the identity of a given paint product. Conditions tested included extremes such as a four day heating period and exposure to 900ºC. Exposure to 900ºC resulted in spontaneous combustion of the paint and is equivalent to an extremely hot house fire, well above typical ignition temperatures. The results of this study therefore demonstrate that even after the endurance of exceptional conditions, a paint sample may still be traced to its original source given the correct database. Furthermore, the colour and manufacturer of the paint could be concluded from the ashed remains.

## CONCLUSIONS

The aim of this project was to confirm and further establish the feasibility of trace element profiling using LA-ICP-MS as a possible identification technique for artists materials, based upon previous work carried out by Horton (2003). Following the analysis of a selection of 45 paint samples, it was observed that each sample could be characterised by a unique trace element profile and that this profile was reproducible given that the conditions of analysis were equivalent. Additionally, it was determined that each individual profile was affected by three independent variables; colour, manufacturer and vehicle type.

Results of a comparative study incorporating data from this analytical protocol and equivalent samples collected in 2003 by Horton indicated that it was possible to correctly classify data of the same paint type, collected in 2003 and 2005, despite an extended period of time between analyses. These findings indicate that ICP-MS instrumentation, although a relatively new technique in the area of artwork authentication has significant potential in this field.

A novel exploration was undertaken to try and emulate the conditions of an arson incident. This was achieved by the controlled heating of samples at temperatures of 200, 400, 600 and 900ºC for varying increments of time. Results for this study indicated that although there was a decrease in the spectral profile match for given samples as temperature and heating interval increased, the results obtained for individual samples remained reproducible and could be traced back to an original source. These results were significant as they indicated that there is not a requirement for the temperature or heating interval of a fire to be known in order to potentially trace the identity of a given paint product.

## FUTURE RESEARCH

The conclusions drawn from this research are limited to the samples investigated. Further studies are required to:

- determine the elemental compositions of traditional and modern artistic media, in order to broaden the content of the developed databases.
- identify and explain differences between the elemental compositions of paint samples and of paint samples applied to a support matrix.
- determine the volatilization of elements as well as the organic composition of modern artist paints.
- investigate the characterisation and subsequent separation of single pigment profiles within mixed palettes so this information can be practically applied.
- investigate the nature of organic and synthetic pigments under conditions of arson.
- investigate separation techniques to allow the division of support media and paint samples. Effective media separation techniques would assist in the removal of support media matrix effects in LA-ICP-MS analysis.
- evaluate organic analysis techniques such as offline pyrolysis gas chromatography mass spectrometry (Py-GC-MS) and high performance liquid chromatography (HPLC) as methods of characterisation for paint samples containing specific binder types and common pigment additives. This line of research may have great potential as a means of identifying, with high confidence, specific manufacturers and paint types.
- study homogeneity of samples derived from the same origin by analysing batch variation.

## MS RACHEL GREEN

***Trace elemental fingerprinting of Australian ochre for the provenance establishment and authentication of indigenous artworks.***

**2004 - Present**

## RESEARCH BACKGROUND

The potential for provenance establishment of ochre has been explored in a number of other projects around the world. Studies conducted into the PIXE, XRD and XRF analysis of ochres have proven useful to some degree. However, these methods are likely to be supplementary to a multi-elemental technique rather than a stand-alone method for complete chemical characterisation, as information on elemental composition and speciation, which alone is not sufficient for provenance purposes. Microscopy techniques such as SEM-EDS, TEM and various adaptations of these were trialled and yielded interesting results. It was found that using these techniques in combination provided an accurate and reproducible method for pigment identification, but without providing information on provenance of the material. A study conducted by Ajo et al (2004) indicated that pigment differentiation was indeed possible using a combination of SEM-EDS and XRD. However, the provenance indication value of these pigments was limited as only large general global areas of origin could be defined and data was not detailed enough to identify specific areas of the world. Spectroscopic techniques, including FT-IR, UV-Vis and Raman have been used for pigment differentiation but with limited success. Bikaris et al (1999) showed that through using spectroscopic techniques differentiation of ochres was indeed possible on the basis of their elemental composition. However the groupings achieved were broad and generalised.

Traditionally, the instrument of choice for provenance determination of artworks has been the optical microscope coupled with x-ray analysis. The latter technique used in both a conventional medical mode and as an analytical instrument often coupled with a scanning electron microscope. Laser ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has not been used at all in this area. While traditional techniques have their use, a significant number of instances occur where definitive provenance establishment cannot be proved and additional corroborative techniques are needed. Multi-element compositional data for artist's materials can provide such support. The chemical composition and manufacturing processes associated with the production of artists media change significantly with time, resulting in variations in chemical signature. Additionally, natural products originating from a specific area have an inherent chemical signature that is characteristic of the source of the material and thus specific to that source. Consequently, relating the chemical composition of both manufactured and natural artist media to the manufacturing or natural source through database interrogation will significantly assist in provenance establishment protocols. LA-ICP-MS has specifications that ideally suit it to this task. It is essentially non destructive, samples take little preparation and extremely small samples can be accurately analysed.

One unfortunate aspect of LA-ICP-MS is that currently it cannot be used to determine the exact quantitative composition of any material. This is due to a number of understood factors that, for some matrices, present an insurmountable problem. However, this is not necessarily true for paints, fixatives and binders. Consequently, research was conducted in order to develop the first methods for the specific quantification of the chemical composition of these materials and to develop a series of robust protocols that may be used to relate the chemical composition of both natural and manufactured pigments to individual artists and art cooperatives thus assisting in the validation and authentication of indigenous works of art. Additionally, a database was developed to be used to assist in the provenance establishment of recovered material.

With the introduction of a portable laser system (Smith 2005) this method may become an ideal way to analyse paintings in situ, with no damage and therefore no reduction in the value of the artwork. Although quantitation remains a problem with ochres, previous research (Green 2004) has shown that for ochres specifically, inter-elemental associations ('elemental fingerprints') are sufficient for discrimination purposes.

Recent research (Horton 2003 and Green 2004) has indicated that provenancing materials commonly found on Indigenous artwork was possible using LA-ICP-MS. Ochres collected throughout Western Australia and the Northern Territory were analysed and matched back both to 'unknown' ochre samples and the artworks produced using those samples. In each case, positive assignment was made and regions were distinguished from one another using the inter-elemental association or 'fingerprint' of the ochre. Although this work was only preliminary, the results were very positive and indicated that the potential existed to provenance materials used on traditional and contemporary indigenous artworks

Ochres consist primarily of iron, silicon, aluminium and manganese, present mineralogically as quartz, hematite, kaolinite and goethite, with potassium, sodium and lithium alumino-silicate inclusions. As ochres are a weathering product of various intrusive rocks, they will also contain the rare earth suite of elements. The distribution pattern of this suite of elements is often site specific to the region from which the ochre was obtained and this geological uniqueness can provide a further means for determination of provenance the ochres.

The mineralogical composition and physical properties of ochres correspond to the physical-chemical conditions of weathering, sedimentation and alteration processes taking place during their formation. These conditions give rise to different types of laterites, ferrolites, ochres and coloured clays and soils, all of which may be used in the production of artworks and all of which are represented in early human art[7]. Structurally and mineralogically, the characteristics of clay minerals and alumino-silicate minerals are directly related to their genesis and provenance and may be used as significant identification features when investigating historical painting techniques and materials.

### Project Objectives

The aim of this research was to develop a robust scientific method to facilitate determination of provenance of Australian ochres and the artworks created using them. Ochre of known provenance was analysed using LA-ICP-MS with assorted data

processing methods including ternary plots, principal component analysis and chondrite normalisation along with search-match procedures. These results were compared and plotted, to visually illustrate population separation of samples based on their chemistry. These differences were identified both between regions and within a single region. The major objective of this project was to determine the trace metal signatures of various Australian ochres in an effort to establish their provenance. This type of research has not been undertaken to date and no reference methodology is available. Consequently, it is necessary to first establish a robust and reproducible analytical protocol. The final sample preparation method must be able to achieve a complete break down of the ochre without contamination or loss of analytes. Analysis of ochre solutions is to be performed using solution based Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Elemental composition data will be employed to establish differences between ochre sites. Laser ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS) will also be employed to analyse the solid ochre samples as the technique is capable of being used to analyse extremely small sample areas and consequently will have application for the analysis of pigment directly on artwork. Laser ablation produces extremely small sampling craters and consequently can be used without significantly damaging a painting. It is envisaged that LA-ICP-MS will be used to associate pigments on artworks to specific areas and schools of art and to specific artists thus assisting in provenancing artworks directly.

## Results

- Ochre samples sourced from different regions within Australia had unique and distinguishable trace metal signatures. The reproducible overlaying of trace elemental signatures for each replicate suggests that laser ablation ICP-MS has excellent application for the analysis and provenance establishment of ochre samples.
- Analytical reproducibility is proof that only a single sample of ochre from a specific site is required to obtain accurate and representative trace elemental concentrations for ochres from that site.
- A single fragment of ochre sampled from an original artwork is sufficiently homogenous for data obtained from its analysis to be used legitimately to establish geographical origin.
- The artwork samples could be related back to ochre samples of the same mineralogy and geological origin.
- Sample powdering procedure had no effect on the trace elemental composition, with the exception of an increased detection of cobalt and tungsten. This increase in specific elemental concentrations is to be expected as incorporation of abraded material from the ring mill results in contamination by these metals. However, the increased levels of these metals do not cause problems with the provenance establishment mathematical protocols and do not lead to false provenance identification, as tungsten and cobalt are not used for provenance establishment purposes.
- Additives, including PVA glue and local Warmun water used to produce the traditional ochre paint, were analysed. The majority of elements were detected at levels approaching the instrumental detection limits. The additives were found to not significantly contribute to the elemental fingerprint of the paint. Therefore, if an ochre sample from an artwork is analysed and the data compared with the data for the original ochre, the inter element association patterns for both will essentially be identical.
- Using various statistical manipulations, all ochre samples analysed so far were discriminated from each other. Furthermore, discrimination within a single region allowed ochre samples collected from within 50km of each other, to be chemically separated. Therefore, once a database is established, an unknown sample may be analysed and determined to have originated from within a 2500km$^2$ area of land. This relates to an extremely specific region when the size of the country is taken into account.
- Further research was conducted to test the validity of the study procedures for provenancing fraudulent artwork. A sample of artwork was analysed together with ochres from various regions across northern Australia. It follows that the materials used on these artworks are of the same origin and thus may be linked through their inter-elemental ratios determined using this technique. A search/match screening protocol was used to determine how comparable the ochres from the Tiwi region were with the artwork sample. From these analyses, the elemental distribution patterns of both the Tiwi Island ochre samples and samples from the artworks were found to match. This proves that they originated from the same source. As such, the utilization of LA-ICP-MS for establishing provenance of artworks through ochre analysis has been established.

## Conclusions

A database of ochres has also been initiated. Although more samples from more regions around Australia are required before it can be put to practical use, ultimately it is hoped that by using this database, ochres may be related back to a particular geographical origin within Australia and artworks can be unambiguously associated with a particular artist. Given the protocol for establishing provenance of ochre samples and in turn artwork samples has been established, the potential to establish a comprehensive database exists. This database, centred on the ochres' specific trace elemental distribution pattern, would facilitate retrospective searching and provenance establishment of existing artworks. The specific 'fingerprint' of the ochre would be stored electronically and compared with similar 'fingerprints' from spatially associated equivalents to establish regional 'fingerprints'.

In this way, identification of regional variations in natural pigments is possible, which can be related back generically to regional art centres. This database could then be used to determine if the ochre on a particular artwork came from the area used by that artist. A specific fingerprint could then be used as evidence of the ochre's identity and origin and its potential association with a regional school of art and artist. Once established, the identity of the ochre may assist the legal process by providing supporting evidence in fraud investigation.

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