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CAN DISPERSED AND MIGRATED ARSENIC FROM DEGRADED PIGMENTS IN PAINTINGS BE A MARKER FOR WATER-LINKED TRANSPORT PROCESSES?

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ABSTRACT

Chemical degradation of emerald green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$) and photo-degradation of orpiment (As_2S_3) and realgar (As_4S_4) in oil paintings have arsenic trioxide (As_2O_3) as a common degradation end product. In such paintings, arsenic is no longer confined to the pigment particles, but is detected with elemental X-ray analysis throughout the whole paint system, e.g., at layer interfaces, in varnishes, around iron- and aluminium-containing particles and in the wood structure of a panel painting. Several case studies are presented. The migrated arsenic is thought to be transported within the paint system as arsenic trioxide in aqueous form by the same mechanism as its transport in groundwater in the environment. Dispersed arsenic in paintings released from degraded pigments can be a marker for water-linked transport processes.

RÉSUMÉ

La dégradation chimique du vert de Véronèse ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$) et la photodégradation de l'orpiment (As_2S_3) et du réalgar (As_4S_4) dans les peintures à l'huile ont le trioxyde d'arsenic (As_2O_3) comme produit de dégradation final commun. Dans ces tableaux, l'arsenic n'est plus confiné aux particules de pigment, mais il est détecté par analyse élémentaire aux rayons X dans l'ensemble du système pictural, c'est-à-dire à l'interface des couches, dans les vernis, autour des particules contenant du fer et de l'aluminium et dans la structure en bois d'une peinture sur panneau. Plusieurs études de cas sont présentées. Lorsque l'arsenic migre, il semble qu'il transite à travers le système pictural en tant que trioxyde d'arsenic sous forme aqueuse par un mécanisme semblable à son transport

INTRODUCTION

Various chemical and physical processes leading to material change take place in oil paintings thus affecting the picture. The effects are diverse and range from discoloration of oil paint to protruding metal soap aggregates and crack formation. Many of these processes require transport of substances through the mature oil paint. For example, migrated fatty acids that form blooms and efflorescent crusts at the painting surface. The transport of substances can take place by diffusion processes or via evaporating solvents introduced by cleaning procedures. In general, the transport processes within the paint system are difficult to visualize but their results are often entirely obvious. This paper addresses the change in the original arsenic distribution, i.e., confined to pigment particles, that results in a dispersed arsenic distribution which points to transport in the aged paint films. Arsenic is primarily transported in ground water in oxide form (Welch 2003) and is therefore a marker for water-linked transport.

Paintings hold a certain percentage of water depending on the relative humidity. This water is not positionally fixed within the painting, but in equilibrium with the environment, thus in motion. Water transport in paint samples is however hard to pin down, as analytical techniques (like imaging-(ATR-)FTIR or NMR-MOUSE) are limited in sensitivity and (spatial) resolving power. Arsenic observed in dispersed form originating from degrading arsenic containing pigments in oil paints could indirectly point to water-linked transport processes. So, the arsenic distribution indirectly shows the water permeability of a painting. This knowledge helps to understand the redistribution of other water transportable components, e.g. potassium, sulfates, oxygenated fatty acids, metal soaps and free diacids etc. *within* the multi-layered paint system. The awareness of the transport processes of water transportable components within the paint system and the permeability of the paint system to polar solvents is crucial for active and passive conservation.

A limited set of pigments contains arsenic (As): emerald green ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$), Scheele's green (CuHAsO_3 , in several chemical compositions), realgar (As_4S_4), orpiment (As_2S_3), some varieties of cobalt violet ($\text{Co}_3(\text{AsO}_4)_2$, $\text{Mg}_2\text{Co}(\text{AsO}_4)_2$) and in smalt (potassium-cobalt-glass) as a minor element. Other sources of arsenic in oil paintings are not known to the authors. Many of these pigments are unstable. Orpiment and realgar

dans les eaux souterraines dans l'environnement. De l'arsenic dispersé dans les tableaux à cause de pigments dégradés est donc un marqueur potentiel de processus de transport liés à l'eau.

RESUMEN

La degradación química del verde esmeralda ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$) y la fotodegradación del oropimente (As_2S_3) y el realgar (As_4S_4) de las pinturas al óleo tienen el trióxido de arsénico (As_2O_3) como producto final común de la degradación. En dichas pinturas el arsénico ya no se limita a las partículas de pigmento, sino que se detecta con análisis de rayos X elemental a través de todo el sistema de pintura, por ejemplo en las interfaces entre capas, en barnices, alrededor de partículas que contienen hierro y aluminio y en la estructura de madera de una pintura sobre tabla. Se presentan varios estudios de caso. Se cree que el arsénico que migra es transportado dentro del sistema de pintura como trióxido de arsénico en forma acuosa, por el mismo mecanismo por el que es transportado en las aguas subterráneas del ambiente. El arsénico dispersado en las pinturas, liberado a partir de pigmentos degradados, puede ser un marcador de los procesos de transporte vinculados al agua.

are photosensitive: orpiment degrades into arsenic trioxide and realgar photo-degrades into pararealgar (West Fitzhugh 1997, Trentelman 1996), which in turn is converted into arsenic oxide (Korenberg 2008). Emerald green is chemically converted into copper soaps and arsenic trioxide (arsenolite, cubic) (Keune 2011).

The arsenic-containing pigments used in oil paints thus have arsenic trioxide as a common degradation product with the exception of smalt and perhaps cobalt violet (degradation products not known to us). In our case studies, an altered distribution of arsenic is demonstrated in several paint cross-sections with scanning electron microscopy combined with energy-dispersive X-ray analysis (SEM-EDX). Our hypothesis of arsenic's water-linked transport derived from these studies will require further studies with reconstructed oil paints with the arsenic pigments mentioned.

METHODS

Scanning electron microscopy studies in combination with energy dispersive X-ray analysis (SEM-EDX) were performed on a XL30 SFEG high vacuum electron microscope (FEI, Eindhoven, The Netherlands) with an EDX system with spot analysis and elemental mapping facilities (EDAX, Tilburg, The Netherlands). Backscattered-electron images of the cross-sections were mostly taken at 20 kV accelerating voltage, at a 6 mm eucentric working distance and a spot size of 3, which corresponds to a beam diameter of 2.2 nm with current density of approximately 130 pA. Prior to SEM-EDX analysis, samples were either carbon coated in a CC7650 Polaron carbon coater with carbon fibre or gold (3 nm thickness) in a SC7640 gold sputter coater (both Quorum Technologies, Newhaven, East Sussex, UK) to improve surface conductivity.

CASE STUDIES

Migration of arsenic deriving from emerald green pigments

Descente des vaches (1834–1835, canvas) by Theodore Rousseau (Museum Mesdag, The Hague) is an oil painting that is currently in very poor condition (Boitelle 2001). Darkening, various cracks and surface deformations affect the appearance of this painting (Van den Berg 2002). The green painted parts of trees and foliage, in particular, have lost their colour and contrast and give the painting a very dark appearance. This painting was painted for the 1836 Paris Salon. Apart from the Salon version, two autographed versions of *Descente des vaches* are known, an oil sketch and a full-scale ébauche version, in which the colours are better preserved. In contrast to the oil sketch and the ébauche version, Rousseau is said to have experimented with drying oils, bitumen (no chemical evidence found) and a megilp-like medium for his Salon version. Many medium rich layers were applied (wet-in-wet), less for reworking of the representation, but primarily to reach a sparkling bright green effect that used the transparency of the paint. A paint cross-section

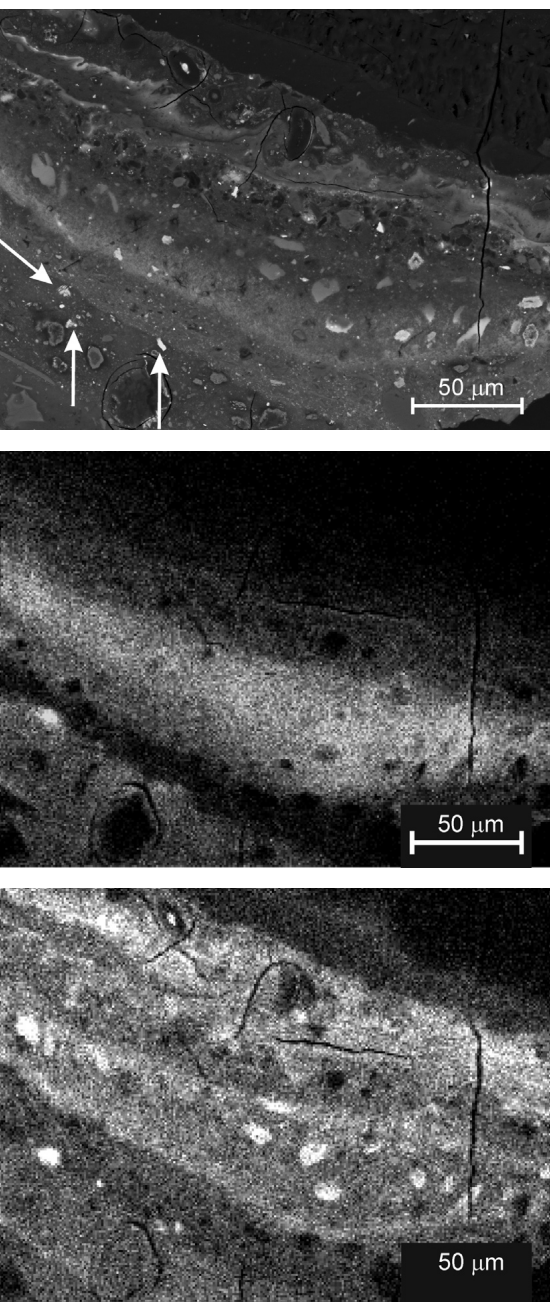


Figure 1

Backscatter electron image showing a detail of a paint cross-section taken from an originally green area in the *Descente des vaches*, Museum Mesdag, The Hague. Arrows indicate remnants of emerald green particles

Figure 2

Elemental distribution of copper (L-line) in a paint cross-section taken from an originally green area in the *Descente des vaches*, Museum Mesdag, The Hague; area corresponds to Figure 1

Figure 3

Elemental distribution of arsenic (L-line) in a paint cross-section taken from an originally green area in the *Descente des vaches*, Museum Mesdag, The Hague; area corresponds to Figure 1

from an area that was initially intended to be green indeed shows a very thick paint package with many (14) different paint layers applied on top of each other. Degradation and alteration reactions must have started at an early stage of drying, since within forty years of its finishing, strong visual changes in the painting's appearance were noticed and it was deemed a lost cause.

The remnants of the main green pigment identified with light microscopy, elemental analysis and Raman spectroscopy is emerald green. Various paint cross-sections taken from *Descente des vaches* show that emerald green is degraded in copper soaps and dispersed arsenic (Keune 2011).¹ Chemical experiments have shown that copper soaps and arsenic trioxide (As_2O_3 , arsenolite, cubic) are formed after two months when emerald green is mixed with fatty acids under slightly acidic conditions at room temperature (Keune 2011).

Light microscopy and SEM-EDX reveal only a few remaining degraded emerald green particles (see arrows) in a paint sample taken from an initially green paint area (Figure 1). The spatial distribution of the elements copper and arsenic is not the same (Figure 2 and 3). Copper – not associated with particles – is concentrated in the paint layers in the middle of the paint cross-section, while arsenic – in dispersed and particle form – is detected in all paint and varnish layers. Emerald green particles are (completely) degraded in this sample. Copper is present in the form of copper carboxylates as identified by imaging-FTIR (Keune 2011). Arsenic is found in relatively high concentrations at the interface between paint layers, around iron- and aluminium-containing pigments and in unidentified (apparently newly formed) particles containing lead, arsenic and oxygen. Arsenic found in the upper and varnish layers seems to be associated with lead and sulphur.

In a second case study, paint samples taken from historic interiors with emerald green paint also demonstrate a redistribution of arsenic. Emerald green was used as green paint on the “Hl. Theresa” cupboard from the master of the Losensteinleitner Werkstätten (1824), Freilichtmuseum Sumerauerhof, St. Florian, Austria. This varnished cupboard is highly decorated. The paint sample taken from the pilaster in the right upper corner is built up with a white clay-containing primary layer followed by a green paint that consists of a mixture with emerald green, barium sulphate and lead white. The backscatter image reveals a relatively compact paint layer with large irregular and crystalline emerald green particles (around 20 micron) as confirmed by Raman spectroscopy (Figure 4). Arsenic is detected by elemental analysis in the emerald green particles and in the varnish layer covering the emerald green paint layer (Figure 5). Emerald green is the only source of arsenic in this paint. Arsenic detected in the varnish layer must be derived from the emerald green particles. Although the emerald green particles seem to be intact in the backscatter electron image, a relatively small quantity of emerald green has reacted away.

Migration of arsenic deriving from orpiment and/or realgar pigments

The presence of arsenic in originally arsenic-free areas is not solely limited to paints with (partially) degraded emerald green pigment. Migrated arsenic is also found in painted works of art where orpiment or realgar pigments are used. One of these paintings is the *Herald* (Southeast) by Christiaan van Couwenbergh (1648–1652, Oranjezaal, The Hague). A yellow highlight on the red jacket consists of orpiment. It is an intact paint layer with elongated flakes of natural orpiment oriented horizontally which points to a slow drying of the oil paint. The paint cross-section is built up of two layers of lead white ground, a red layer composed of vermilion and red lake, and a final layer with orpiment (Van Loon 2006). Elemental spot analyses detected arsenic in the red layer (vermilion mixed with red lake) as well as in the lead white-containing ground (spectrum not shown).

Two other examples illustrate the altered distribution of arsenic in degraded orpiment/realgar-containing paints. *Still life with five apricots* by Adriaen de Coorte (1704) (The Hague, Royal Picture Gallery Mauritshuis) is a small oil painting on canvas (Pottasch 2010). The painting has a thick yellow ground layer pigmented with yellow and red ochre, chalk, sienna and umber. The apricots are painted with a light orange paint composed of orpiment and/or realgar and gypsum, which is probably present as an extender or as the substrate of a yellow lake. On top, a bright red vermilion-containing layer is present with red glazes and white highlights. The apricots show degradation phenomena characteristic of degraded orpiment/realgar-containing paints,² i.e., very crumbly paint, especially along the cracks, and a high sensitivity to moisture during conservation treatment.

The paint sample taken after varnish removal from one such degraded area in one of the apricots is built up with a thick ground layer (250 micron) and a degraded paint layer with yellow and orange orpiment/realgar particles (60 micron) (Figure 6). The upper part of the realgar/orpiment layer (20 micron) has been degraded under the influence of light. The light microscopic image reveals a paint layer with a translucent orange upper part and a more yellow/orange opaque lower part. Under UV-light, the upper part is highly fluorescent with few orange particles, while the lower part shows a densely packed layer of orange particles (Figure 6). Backscatter electron imaging reveals a mixture of large angular realgar/orpiment particles (up to 20 micron) with smaller flake-like particles (Figure 7). Realgar/orpiment particles are lacking in the upper part, while the lower part is still intact (Figure 7). It is clear that the upper part is photo-degraded. Partially degraded realgar/orpiment particles are visible in the upper part (see arrow, Figure 7) with a crumbled upper edge (side exposed to light), while the lower side of the particles are still intact (sharp edge). Additionally, tiny particles are visible where the core is intact, but the rim edges are undefined and fuzzy in the backscatter image. Furthermore, the backscatter image reveals dark “gaps” in the gypsum

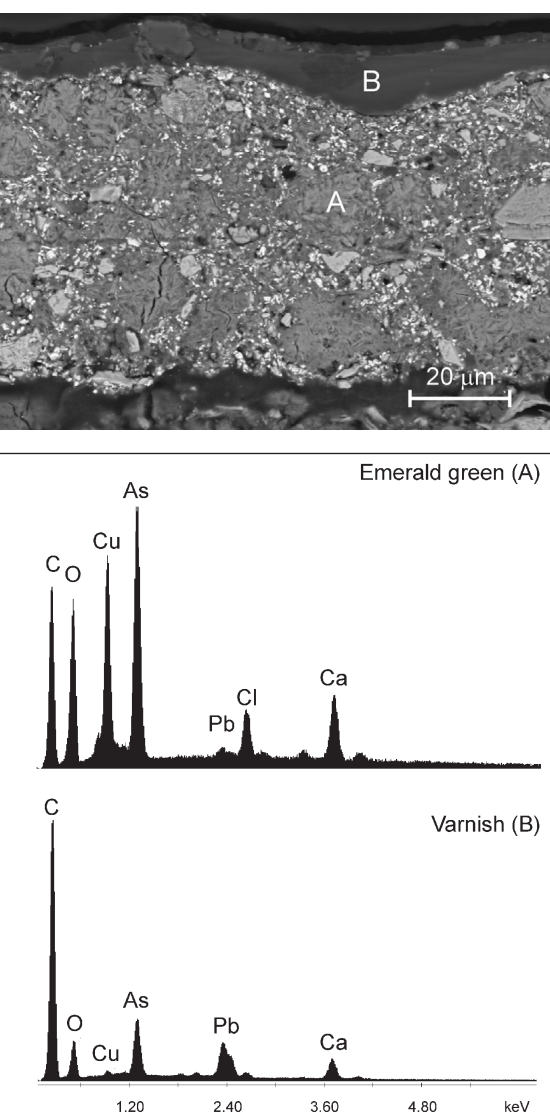


Figure 4

Backscatter electron image showing a detail of a paint cross-section taken from a green decoration in the cupboard “Hl. Theresa” from the master of the Losensteinleitner Werkstätten

Figure 5

Elemental X-ray spectrum of emerald green particle (A) and varnish (B); spot of analysis (A and B) is indicated in Figure 4

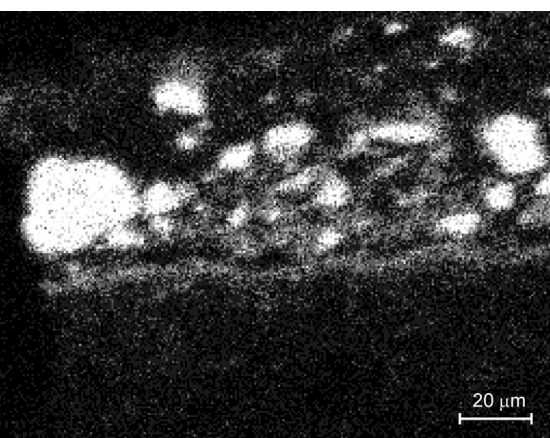
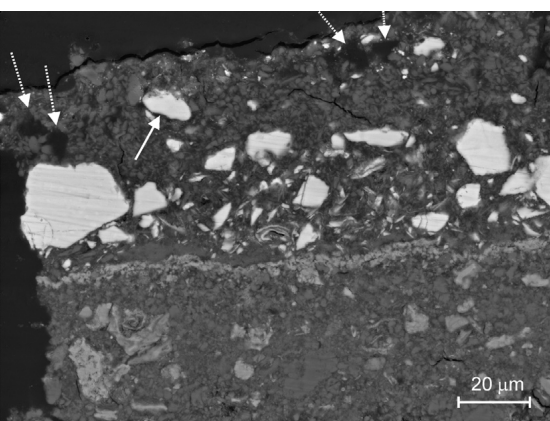
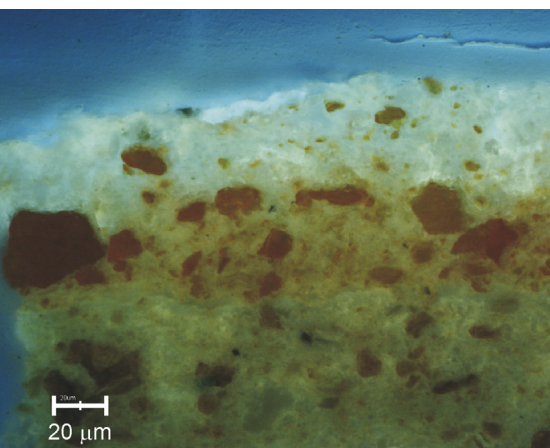


Figure 6
Light microscopic image of paint cross-section of *Still life with five apricots*, Mauritshuis, The Hague, under ultraviolet light conditions

Figure 7
Backscatter electron image showing a detail of a paint cross-section taken from *Still life with five apricots*, Mauritshuis, The Hague

Figure 8
Elemental distribution of arsenic (L-line) in a paint cross-section taken from *Still life with five apricots*, Mauritshuis, The Hague; area corresponds to Figure 6 and 7. The arrow indicates a partially degraded realgar/orpiment particle, the dotted arrows indicate "gaps" in the paint matrix

matrix of the degraded part (see dotted arrows, Figure 7). These gaps have the shape of realgar/orpiment particles. The gaps are interpreted as remnants of lost degraded realgar/orpiment particles. Arsenic is present at the interface between ground and paint layer in a relative thick layer with a medium electron backscattering intensity (Figure 8). Arsenic is precipitated at the top of the iron-containing ground (iron compounds have a high affinity for arsenic trioxide). Arsenic is also detected in the bulk of the ground with higher concentrations in the iron-containing pigments by elemental X-ray spot analysis. The relative concentration of arsenic in the ground layer and in the iron-containing pigments is too low however to visualize in the arsenic map (Figure 8). Evidently, the arsenic-containing degradation products have not remained in their original position, i.e., the pigments, but have migrated and are now deposited at the interface between ground and paint layer and in the ground layer. As varnish is lacking in this sample, it cannot be verified whether arsenic also migrated upwards. However, the arsenic map reveals a relative increase of arsenic near the surface (Figure 8).

The Dentist, attributed to an unknown 17th-century artist, is an oil painting on panel (private collection). The pictorial image of *The Dentist* is a reproduction of Lucas van Leyden's engraving *The Dentist* (1523, Rijksmuseum, Amsterdam). A paint sample taken from the orange skirt of the woman at the right has a build-up of a chalk-lime ground with a transparent brown umber or Kassel earth-pigmented brown second layer with lead white, and a layer with a carbon-black pigmented underdrawing. The three paint layers are a red layer pigmented with vermilion and red lake (chalk substrate), a densely packed orange layer with realgar and a lighter orange layer with a mixture of realgar and gypsum (present as an extender or substrate for a lake).³

The angular realgar particles (1-5 micron) are mainly present in the lower part of the lighter orange layer where compact packed individual orange realgar particles are sometimes hard to distinguish and a greyish undefined interlayer near the bottom of the layer is visible. Comparison of the paints in *The Dentist* with those in *Still life with five apricots* supports the interpretation that the appearance of the realgar-containing layer in *The Dentist* is the result of the photo-degradation.

Relatively low concentrations of arsenic originating from the realgar are detected in the wood and paint layers with elemental spot analyses. The elemental map of arsenic reveals slightly higher arsenic abundance in the iron-containing pigments in the transparent brown second layer compared to the other paint layers and the wood fibres.

DISCUSSION

The examples given justify the idea of active transport of arsenic within the multi-layered paint system. It is not very likely that the pigments themselves migrate through the paint system. Our hypothesis is supported in the case of the emerald green containing paints by the fact that only

arsenic and not copper is detected in the originally arsenic-free areas. In the case of realgar/orpiment, only arsenic and no sulfur is detected in the ground of *Still life with five apricots* and the wood of *The Dentist*. Arsenic trioxide was the only degradation end product of emerald green in experiments where the pigment was degraded by fatty acids into copper soaps (Keune 2011). Arsenic trioxide is one of the end products of the photo-oxidation of realgar and orpiment (Dubois 2001)

The redistribution of dispersed arsenic is evidence of the migration of arsenic presumably in the form of arsenic trioxide within the painting. Arsenic trioxide slowly dissolves in water and is stable under neutral and weakly acidic pH and under moderately reducing conditions (Welch 2003, O'Day 2006). Solubility of arsenic trioxide (amorphous) is 37 gram/liter in cold water (Weast 1979) which makes water-linked transport feasible while migration of pure arsenic trioxide is not likely as the melting point is very high (mp. 312°C) (Weast 1979). Arsenic trioxide (an aqueous form of H_3AsO_3) has a strong sorption affinity for iron hydroxides and iron oxyhydroxides (such as goethite). Other minerals like clays, aluminium oxyhydroxides and manganese oxides also absorb arsenic trioxide (Welch 2003, O'Day 2006). This behaviour of arsenic trioxide corresponds with the observation of relatively higher arsenic X-ray fluorescence intensities around iron- and aluminium-containing pigment particles in *Descente des vaches* and in iron-rich layers in *The Dentist* and *Still life with five apricots*. It is possible to conclude from our observations and the cited physical data that the arsenic is transported within the paint system of our case studies as arsenic trioxide in aqueous form (H_3AsO_3). Water-linked transport in paintings has far reaching implications beyond the paints where arsenic from degrading arsenic containing pigments can be used as tracer. On a molecular level, a painting can be seen as a nanoporous system which is accessible for water. Water can be transported by diffusion or along micro cracks following the craquelure system driven or sustained by gradients in relative humidity, temperature or airflows. Arsenic in the arsenic oxide form appears to be a good tracer for water-linked transport. So it may be possible to use it in experiments investigating the role of water molecules in the transport and migration of other substances in paintings.

CONCLUSION

Arsenic was found out of place in several works of art in which paints with arsenic containing pigments had been used. Arsenic can be transported as arsenic trioxide in aqueous form (H_3AsO_3). On the basis of the detection of arsenic in originally arsenic-free painted areas it is concluded that water plays a role as a transport medium within the painting. Although arsenic is seen as a marker for water-linked processes, in the paintings under study presented here, we propose that water-linked transport is a general phenomenon that would explain many other material transport phenomena in paintings.

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NOTES

- ¹ This paper focuses on the reaction chemistry in experimental studies of reference materials and occurrence of reaction products in paintings.
- ² Personal communication of senior conservator C. Pottasch, Royal Picture Gallery Mauritshuis.
- ³ Realgar is determined on the basis of light microscopy and elemental analyses in paint cross-sections.

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