Binding medium, pigments and metal soaps characterised and localised in paint cross-sections
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Chapter 1

Introduction
1.1 Studies of paint cross-sections

Paintings are composed of heterogeneous mixtures of organic and inorganic compounds with an often complex multi-layered build-up. Analytical studies of paintings performed on the microscopic and molecular level are the focus of this thesis. The relevance of such an investigation of paintings is the identification of materials to solve art technical historical questions, the deduction of the original appearance and the establishment of the chemical and physical condition before restoration and conservation. Microscopic and molecular studies are carried out on tiny paint samples derived from the painting. These tiny samples are unique and in limited supply. Assuming that such tiny samples are representative for an area under study, valuable general information about the painting can be deduced. The information can be maximized by sequential analyses using different complimentary techniques.

Paint scrapings are used for micro-chemical tests and polarized light microscopy to identify pigments. Mineral phase composition of the pigment is determined with X-ray diffraction (XRD). High performance liquid chromatography (HPLC) is now common for the identification of organic pigments. Analysis of paint scrapings with conventional mass spectrometric techniques, such as direct temperature resolved mass spectrometry (DTMS) and gas chromatography/mass spectrometry (GC/MS), gives detailed information on lipids, proteins and resins as constituents of binding medium and varnish. The disadvantages of these types of methods are, however, that positional information is lost, and that the valuable paint sample must be sacrificed.

Since the mid 20th century paint samples are embedded in a resin and polished until a flat cross-section of the multi-layered system, the so-called paint cross-section, is visible. In this manner the stratification of the painting and the distribution of the pigment and medium within the layers are preserved. Chemical tests applied in situ on paint cross-sections will give some pigment information. However, spot tests are hard to carry out accurately; and the sample is modified after testing. Furthermore, chemical spot tests applied to a paint cross-section are limited to the identification of only a few components. Distributional information has to be obtained by extrapolation. Spot analysis with a scanning electron microscope (SEM) combined with energy dispersive X-rays analysis (EDX) provides information on the elemental composition of pigments. The elemental composition obtained is indicative for certain pigments, but pigments with different mineral phases, but the same elemental composition, like lead carbonate or lead hydroxycarbonate cannot be discriminated nor is it possible to identify pigments with an organic composition, like red lakes of madder or cochineal, in
this manner. Additional analytical techniques have to be applied to the paint cross-section in order to obtain this information. Mineral phases can be determined with XRD and in paint cross-sections, imaging-XRD could be done with electron backscatter diffraction (EBSD), but this technique has not yet been applied successfully for paint cross-sections, because the surface cannot be made flat enough with the present polishing techniques. So in contrast to rock samples, the various mineral phases present in paint cross-sections cannot be visualised up to now. So far, the elemental composition is used as indicator for the inorganic pigments in paint cross-sections. For identification of organic pigments the combined information from colour, fluorescence, particle shape and elemental composition (for instance elements representative for their substrates) is indicative.

Information on the molecular composition cannot be obtained easily from paint cross-sections. The organic chemical composition of paint cross-sections, e.g. the demonstration of proteinaceous and oleaginous binding media, can be visualised with staining techniques. However, factors like heterogeneous chemical composition of the medium, ageing processes, the interference with certain pigments, the infiltration of the stain in the cracks or porous layers can easily contribute to a false positive or negative staining results. Furthermore, staining tests are irreversible. Staining is an indirect method to identify the organic composition and the outcome is limited to the selected stain. The exact molecular organic composition and unexpected organic compounds cannot be identified in this way. Potential molecular identification techniques are imaging Fourier transform infrared spectroscopy (FTIR) and the mass spectrometric imaging technique of secondary ion mass spectrometry (SIMS). These imaging techniques are not generally accessible in conservation studios or museums. The advantages and limitations of these techniques for painting studies will be addressed in the forthcoming paragraphs.

The disadvantage of several of the methods addressed above is that the results are limited to the characterisation of the materials while positional information is missing. Besides, in most cases only a single analysis can be carried out on the paint sample, because the precious sample is damaged or lost in the process. To identify painting materials on a molecular and elemental level, these advanced analytical imaging techniques are required. Since there is no single technique, which is informative about all aspects of pigments and binding media, several analytical imaging techniques have to be applied together to reveal "all" aspects of the paint composition. In our laboratory the surface of the paint cross-section is investigated with FTIR, SIMS and SEM/EDX. SIMS is introduced as a new technique for painting research and its usefulness is explored in this thesis. The strength of the combination of these tech-

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niques is that they result in different types of chemical information, which makes them complementary. The techniques are superficial, non-destructive and the same paint cross-section can be investigated with more than one imaging technique. The molecular and elemental images obtained can be overlaid and the combined information results in a rather unique and complete picture of the molecular and chemical composition of the paint layers. For a good comparison of the obtained images the paint cross-section is first subjected to FTIR-imaging and SIMS before SEM/EDX, as this latter technique requires a thin carbon coating. The carbon coating can be polished off for subsequent analyses, but this will change the distribution of materials at the surface. Other imaging techniques relevant for painting studies, like imaging Raman spectroscopy and imaging UV/VIS spectroscopy, are not employed in this thesis, but can be very useful in certain cases.

1.2 Analytical imaging techniques

FTIR-imaging gives information on the distribution of specific chemical functional groups. For example, carbonates (derived from pigments) and carbon-hydrogen bonds (derived from medium or varnish) can be characterised and localised in paint cross-sections. Every measurement in FTIR-imaging yields a completely independent IR-spectrum for every spot on the surface of the paint cross-section with a fast IR-camera. The spatial resolution is limited to about 7 µm and the detection of the camera ranges between 4000 - 1000 cm⁻¹, which implies that characteristic features below 1000 cm⁻¹, such as lead chromate (at 856 cm⁻¹) cannot be identified and imaged. Basic lead carbonate cannot be distinguished from lead carbonate due to the detection range (characteristic peaks are found for lead carbonate at 838 cm⁻¹ and for basic lead carbonate at 778 and 680 cm⁻¹). FTIR-imaging of paint cross-sections as such is restricted to a specular reflectance approach due to the thickness of the sample. The reflectance intensity is determined by the difference in refractive index between two materials (n₂/n₁) described by Fresnel’s law. Minerals or other inorganic materials in paints have a high refractive index ratio, which leads to intense specular reflections (25% with n = 2) and an intense signal in the FTIR reflectance spectra. The opposite is true for organic materials, which results in low intensity signals (4% with n = 1.5) in the spectra. FTIR is able to image pure organic compositions, but the surface must be totally planar in order to obtain good reflections. Unfortunately, when organic compounds are mixed with large amounts of inorganic matter, like chalk or lead white, the peaks representative for the inorganic composition
predominate in the FTIR spectrum. Often, the organic constituent in, for instance a chalk layer, is not visualised with FTIR, as its reflectance and relative concentration are low. Besides in a heterogeneous layer the signal is reduced due to scattering of the infrared light within the sample. Kramer-Krönig transformation is applied to the specular reflectance spectrum to transform it into an absorbance like spectrum, which is more workable and easier to interpret.

SEM is an established technique in technical painting studies. Separate layers, pigment particles and organic constituents can be visualised well in paint cross-sections. The backscattered electrons (BSE) enable a good compositional contrast within the paint cross-section, because heavy elements with high atomic numbers result in higher electron back scattering than lighter elements. Electron beam induced X-rays analysed with an energy dispersive detector (EDX) results in a semi-quantitative spectrum of the elements in the paint cross-section. Elemental mapping gives information on the distribution of these elements in and between the particles in the paint layers. Not all elements can be detected with EDX, because the detection threshold is relatively high and the X-ray energies of several elements overlap. In general, light elements, for example nitrogen, in low concentrations are hard to detect with EDX. EDX is not a suitable technique for detection of trace elements in pigments and media, because their concentration is often below the detection limit (the detection limit is approximately 0.1 wt% for pure materials and is dependent on the element, matrix composition and instrumental settings). Besides, the chance that the generated X-ray radiation is absorbed by lighter elements positioned in the sample is rather large. This is one of the main reasons why quantitative analysis of these very heterogeneous paint samples is barely possible. Elements with overlapping X-ray energies are for instance the K-shell of sulphur with the M-shell of lead. Lead can be identified by its L-shell X-rays. Plotting a theoretical fit by selection of certain elements (an option in the EDAX Genesis soft program) over the acquired spectrum makes it possible to deduce the presence and absence of overlapping elements.

The surface quality of the paint cross-section determines the quality of the BSE-images. A highly flat surface results in better contrast in the images and a sharper visualisation of pigment features at high magnification. The spatial resolution of SEM equipped with a field emission source is about 1-5 nm, this resolution is however rarely required for the study of paint cross-sections. The penetration depth of the beam is determined by the composition of the materials. The dimensions of the interaction volume (volume created by interaction of the primary electron beam with the sample surface) for a low-density and low atomic number specimen are larger \(i.e.\) more pear shaped) than for a specimen with high-density and high atomic numbers.

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So the depth resolution for the back scattered electrons is between 10-1000 nm (dependent on the acceleration voltage of the electron beam), whereas the X-rays are generated in the bottom part of the interaction volume. As the interaction volume is dependent on the composition under study and the beam settings, the correct interpretation of the BSE and X-ray images is very critical. The information deduced from BSE images can be derived from regions positioned below the surface. Elemental information acquired from a particle or area can be mixed with elemental information from its environment. Selecting the proper beam settings for the paint cross-section under study, like low acceleration voltage or small spot sizes, can help interpretation. The paint cross-sections are charge compensated by covering the surface with an ultrathin carbon coating.

SIMS is a surface sensitive technique that uses a high-energy primary ion beam to generate secondary ions from the surface. Elemental, small and larger molecular information can be obtained in this way. Hence, the size and distribution of pigment particles, the position of organic constituents and the interaction between both can be studied in detail in this manner. Scanning of the focussed beam over the surface generates an image. An entire mass spectrum is acquired for every pixel in the image. By selecting a mass of interest, this information can be plotted into an image illustrating the spatial distribution of that mass peak. The advantage of SIMS applied to paint cross-sections is that the distribution of pigment and binding medium can be studied at the same time in a single sample. The spectral mass information obtained can be highly informative about the material composition in the cross-section. The lateral resolution in an image is, depending on the image size, about 1 μm. The depth probing in SIMS is restricted to the upper atomic layers of the sample. SIMS applied to paint cross-sections has some restrictions. The binding medium in paint is a random three-dimensional cross-linked network, which means that ionisation with the primary ion beam leads to fragmentation of the network. The smaller hydrocarbon fragments (< 100 amu) are the most abundant peaks in the spectrum, but they are too common and cannot be used as markers for the binding medium. Ion yields of characteristic fragments of the medium, like fatty acids derived from an oil binding medium, can be low. This can be explained by the fact that only a small fraction of the analysed surface area contains binding medium constituents while the binding medium itself contains only a small fraction of fatty acids. Besides the ionisation and emission efficiency of fatty acids is low. The absence of peaks characteristic for medium can also be explained by instability under the ionisation conditions, which is the case for dicarboxylic acids, an important major constituent of the oil network. Elements like lead, silver and gold not only enhance the ionisation of organic compounds, but also
suppress the fragmentation of e.g. the dicarboxylic acids (see chapter 3.3). This implies that fatty acids are often detected in relative high yields in lead white-containing layers, on lead white particles or near the gold leaf of gildings. The presence of fatty acids in lead deficient layers can therefore not be excluded. This problem can be overcome by homogenizing the surface with an ultrathin metal coating. The benefit of a metal coating is that the ion yields from organic constituent are enhanced, but a disadvantage is that the ion yields from inorganic elements are suppressed, which results in poor quality images.

The advantage of SIMS applied to paint cross-sections is that trace elements, which cannot detected by EDX due to their low concentration, are often detected by SIMS. SIMS has been shown to be able to detect 0.001 wt% of calcium in a lead white matrix, whereas the detection limit of EDX was 0.1 wt% for the same sample (unpublished results). The detection limit of elements in SIMS is depending on their ionisation potential and possible matrix effects. For example, chlorine ionises relatively well, while the ionisation potential of mercury is rather high. The quality of the surface of the paint cross-section is very crucial. SIMS is very sensitive to unevenness of the surface. Uneven sample surfaces result in poor mass and spatial resolution of the SIMS data. The sample preparation must be as clean as possible. Surface contamination with poly-di(methyl)siloxanes and di-iso-octylphthalate must be prevented. Therefore, the samples are rinsed with hexane prior to analysis.

The analytical imaging techniques require a flatter surface of the paint cross-section than what is made available by museums and private restorers. An optimized systematic dry-polishing method was developed to overcome this problem in which the surface is planar; scratches, smearing and holes are minimised and higher quality analytical data are obtained. The sample is fixed in a homemade polishing holder to provide an even pressure on the sample during polishing. The surface area around the sample is decreased to reduce the risk of smearing the embedding medium or certain fractions from the paint itself over the sample. Very short straight movements prevent possible friction, smearing and heating. After each polishing movement the holder is turned by 90°.

During and after sample preparation, contamination is prevented as chemical information must be retained on/in the surface. No liquid to saturate the surface and to reduce the light scattering with the object to improve light microscopic investigation is used on the surface of paint cross-sections. The sample surface is never touched, as fingerprints are a source for fatty acids that are constituent of the oil binding media. A silicone-based putty often used to attach the sample to an objective glass for light microscopic investigations is not used.
1.3 Chemical changes in paintings

The chemical information obtained with analytical imaging techniques gives information about the current composition of the paint sample. It is important to understand that paintings are not static objects, but undergo many chemical and physical changes over time. Original components may be reacting away and new compounds can form. In the past, the conditions for keeping the paintings were not always optimal. Paintings were exposed to fluctuating temperatures, direct sunlight and extremes in humidity, which influenced and promoted chemical aging and degradation reactions in paints. Besides, the various restoration treatments might have influenced the chemical and physical condition of the painting. Spatially resolved analyses of paint cross-sections are expected to give more insight into the time frozen chemical and physical processes, which have taken place.

Many degradation phenomena of pigments are investigated and elucidated via paint cross-sections. Light sensitive pigments degrade on the surface of the painting, but in cross-section a degraded and intact part is visible. As the paint cross-section reveals degraded and intact pigments, the degradation phenomena can be studied in this manner. Examples of pigments which degraded on the surface of the painting are:

![Image of Backscattered electron image revealing an ultramarine particle embedded in a lead white paint matrix. The ultramarine is part of a paint cross-section (A166/1b) taken from the virgin's blue robe in the panel painting 'The Descent from the Cross' by Rogier van der Weyden (1399/1400-1464). The particle has a heterogeneous composition, where its centre has a lower backscattering intensity compared to the edges of the particle. EDX spot analyses reveal a different elemental composition for the centre and edges of the particle. Natural ultramarine (Na,Ca)-(AlSiO₄)(SO₄,S,Cl) is shown in the centre while the edges are proposed to be diopside (monoclinic pyroxene, MgCaSi₂O₆), a mineral associated with lazulite.]

Fig 1.1 Backscattered electron image revealing an ultramarine particle embedded in a lead white oil paint matrix. The ultramarine is part of a paint cross-section (A166/1b) taken from the virgin's blue robe in the panel painting 'The Descent from the Cross' by Rogier van der Weyden (1399/1400-1464). The particle has a heterogeneous composition, where its centre has a lower backscattering intensity compared to the edges of the particle. EDX spot analyses reveal a different elemental composition for the centre and edges of the particle. Natural ultramarine (Na,Ca)-(AlSiO₄)(SO₄,S,Cl) is shown in the centre while the edges are proposed to be diopside (monoclinic pyroxene, MgCaSi₂O₆), a mineral associated with lazulite.
the fading of red and yellow lakes, indigo, the whitening of bone black, blackening of vermilion (see chapter 4), colour changes of chrome and cadmium yellow and the decomposition of orpiment and realgar. Pigments that degrade under the influence of their local external environment can only be visualised in paint cross-section. For example, analytical imaging studies on a partially degraded smalt particle (a blue potash glass) containing a discoloured rim and an intact blue core, indicate that an elemental exchange between the particle and surrounded medium occurred.

The type of binding medium constituents detected in a paint cross-section gives information about the condition of the oil. For example, oil paint with a relatively large amount of metal soaps and a relatively small amounts of free and ester-bound fatty acids is indicative for a mature oil paint. The ratio between two fatty acids - palmitic and stearic acid - can be indicative for the type of oil used in the paint. This ratio is determined from paint scrapings with GC/MS. For a meaningful identification of the type of oil paint, the various layers of the paint sample have to be separated, which is not easy at all or simply impossible. SIMS offers the opportunity to measure this ratio from a paint cross-section (see chapter 3.2). The analytical imaging studies of paint cross-sections result in compositional data on single paint layers in a multi-layered paint system.

From the defects observed in paintings it is clear that pigment and binding medium cannot be seen as two separate components in paint. Certain pigments, like smalt, degrade in an oil medium while they are stable in other media. Small crater-like holes filled with a whitish and opaque material, so-called protrusions, are observed on the surface of many paintings. A protrusion is an aggregate of metal soaps, a reaction product from pigment and oil medium. The process of formation of this defect is deduced from detailed studies of paint cross-sections, as many stages of this phenomenon are often observed (see chapter 5).

In general, the particle, molecular and elemental composition within a paint layer is not homogeneous. This heterogeneous composition within and between layers is informative for alteration and degradation processes that have taken place in the paint. Fig. 1.1-1.3 illustrate that not only paint layers are heterogeneous, but that also pigments can be impure and can have a variable morphology. The figure captions explain the phenomena observed.
Fig 1.2 Backscattered electron images (A) of a slightly corroded lead piece from a ceramic pot (labeled "C") in possession of Old Holland Paint Company (sample nr. OH.10; provided by Dr. I. Carlyle). Traditionally prepared lead white was using the stack process, or "Dutch" method. A sheet of metallic lead in a ceramic pot is exposed to vinegar, carbon dioxide, oxygen, humidity and high temperatures in a pile of horse manure. The metallic lead is converted into lead acetate and subsequently in lead hydroxycarbonate, which is scraped off. The higher magnified backscattered electron images B-E illustrate the different morphologies in different locations on the lead pieces (different levels in the corrosion). The position of images B-E is indicated in image A. The crystals in image C are probably positioned closer to the metallic lead, whereas the crystals in image B derive from the outer surface of the corroded piece. Traditional lead white pigment is clearly not a pure homogenous compound.

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Fig. 3 Backscattered electron image of a lead-tin yellow particle (higher backscattering intensities of tiny lead stannate particles) with tin oxide inclusions (lower backscattering intensity) present in paint cross-section HSTB 12:2001/89. The paint cross-section is taken from a ‘Green Leaf of Allegory on the Marriage of Frederick Hendrik and Amalia van Solns’ by Gerard van Honthorst (1651). Oranjezaal of the Royal Palace Huis ten Bosch (The Hague. The Netherlands) The tin oxide is probably an unreacted residue in the lead-tin yellow pigment as a result of a poorly designed production process. To get a complete conversion of the lead and tin oxides to lead stannate (lead-tin yellow pigment type I), the conditions in the melt are crucial. (backscattered electron image: Annelies van Loon, AMOLF).

1.4 Scope of this thesis

The scope of the thesis is to characterise and localise the constituents of traditional oil paints in paint cross-sections. Oil-containing paint is selected as focal point, because oil is one of the most used binding media in paintings. Besides, the defects described in chapter 5 are associated with the oil medium. The various analytical imaging techniques are used to map characteristics of the oil medium, pigments and their interactions with a high spatial resolution. The analytical imaging techniques are complementary. Examination performed with the various imaging techniques leads to a better understanding of the chemical composition and distribution in paint layers.

In chapter 2, SIMS is introduced as an analytical technique for technical research of paintings. SIMS was performed on a paint cross-section taken from the virgin’s blue robe in the panel painting The Descent from the Cross (Museo del Prado, Madrid) of the Early Netherlandish artist Rogier van der Weyden (1399/1400-1464). This 15th century panel painting is in a very good condition, which makes it an interesting sample for a detailed study of the binding medium, the pigments and their interaction. The SIMS results are supported by and in agreement with the results obtained with light microscopy, imaging FTIR and SEM/EDX. The interpretation of
the secondary ion peaks that are characteristic for the binding medium is verified with the spectrum of reference materials.

Chapter 3 addresses the oil binding medium in paint cross-sections studied by SIMS. Three aspects of SIMS applied to paint systems are presented in this chapter: the identification of mass spectral data, the localisation of characteristic spectral data and improvement of ion yields from organic substances. In the first part of chapter 3, the mass spectral data of SIMS obtained from an oil model system is compared with information obtained with conventional mass spectrometric techniques, like DTMS and GC/MS. In the second part, the spatial distribution of oil paint characteristics, like fatty acids, is presented. The type of fragment ions detected gives information about the chemical condition of the oil paint. The ratio between palmitic and stearic acid can be indicative for the type of oil. The third part addresses a gold-coating method to enhance the ion yields, which are necessary to improve the quality of the images representative for the oil derived components.

Chapter 4 sheds new light on the well-known phenomenon of the blackening of vermilion. The combination of light microscopic images from SIMS and SEM/EDX elucidates the light induced degradation of vermilion. SIMS and SEM/EDX give complementary elemental information and SIMS has the benefit that fragments of inorganic complexes can be detected. This information leads to a proposal for a mechanism of the chloride induced degradation of vermilion.

The interaction between lead- and zinc-containing pigments and the oil medium, which leads to serious defects in the paint film is presented in chapter 5. Many paintings are found to be affected by metal soap formation, which leads to aggregate formation in the paint film and changes in the appearance of the painting. In this chapter, ten case studies are performed using light microscopy, imaging FTIR, SEM/EDX and SIMS. The analytical imaging results give a better understanding of important reactive compounds, paint compositions and external factors relevant for the formation of the metal soap aggregates.

1.5 Publication list

This thesis is based on the following publications:

**Chapter 2**

Chapter 3.1
K. Keune, E. Ferreira and J.J. Boon, SIMS characterisation of traditional oil paint: comparative studies with DTMS and GC/MS, in preparation

Chapter 3.2
K. Keune, E. Ferreira and J.J. Boon, Characterisation and localisation of the oil binding medium in paint cross-sections using imaging secondary ion mass spectrometry. In: Conference Proceedings 14th Triennial Meeting of the ICOM Committee for Conservation in the Hague, September 12-16, 2005

Chapter 3.3

Chapter 4
K. Keune and J. J. Boon, Analytical imaging studies clarifying the process of the darkening of vermillion, accepted for publication in Analytical Chemistry, 2005.

Chapter 5
K. Keune, P. Noble and J.J. Boon, Chemical changes in lead-pigmented oil paints: on the early stage of formation of protrusions, In: Proceedings of ART 2002, the 7th international conference on non-destructive testing and microanalysis for the diagnostics and conservation of the cultural and environmental heritage, R. van Grieken, K. Janssens, L. Van’t dack and G. Meersman (Eds.), Antwerp, Belgium, 2002, 9 pages


**Other publications**


In Press

J. J. Boon, K. Keune and J. Zucker, Imaging analytical studies of lead soaps aggregating in preprimed canvas used by the Hudson River School painter F.E. Church, Microscopy and Microanalysis 2005

J.J. Boon, E.S.B. Ferreira and K. Keune, Imaging analytical studies of Old Master paints using FTIR, SIMS and SEMEDX of embedded paint cross-sections, Microscopy and Microanalysis 2005

A. van Loon, K. Keune and J.J. Boon, Improving the surface quality of paint cross-sections for imaging analytical studies with specular reflection FTIR and Static-SIMS, Conference Proceedings Art 2005, Lecce 16-19 may, 2005


1.6 References

8 J.D.J. van den Berg, K.J. van den Berg and J.J. Boon, Determination of the degree of


14 M. Johnson and E. Packard, Methods used for the identification of binding media in Italian paintings of the fifteenth and sixteenth centuries, Studies in Conservation, 16 (1971), 145-164.


25 A. van Loon, K. Keune and J.J. Boon. Improving the surface quality of paint cross-sections for imaging analytical studies with specular reflection FTIR and Static-SIMS. submitted to Art2005: 8th International Conference on Non-destructive Testing and Microanalysis for the
Diagnostics and Conservation of the Cultural and Environmental Heritage.


35 J.J. Boon et al., *Molecular aspects of mobile and stationary phases in aging tempera and oil paint films*, In: Early Italian Paintings: Techniques and Analysis, T. Bakkenist, R. Hoppenbrouwers and H. Dubois (Eds.), Stichting Restauratie Atelier Limburg (SRAL), Maastricht, 1996, p. 35-56.


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