

Raman Spectroscopy Applied to Iron Oxide Pigments from Waste Materials and Earthenware Archaeological Objects

by

Malebogo Andries Legodi

Submitted in partial fulfillment of the degree

PHILOSOPHIAE DOCTOR

in

CHEMISTRY

in the faculty of Natural and Agricultural Sciences of the

UNIVERSITY OF PRETORIA
PRETORIA

Promoter: Prof. D. de Waal

2008

Declaration of oath

I, Malebogo Andries Legodi, the author of the present thesis entitled “Raman Spectroscopy Applied to Iron Oxides from Waste Materials and Earthenware Archaeological Objects” declare that the thesis contains only original work and that all the results included were generated by the author.

Signature:.....

Date:.....

Acknowledgements

The author wishes to express sincere gratitude to the following:

- Almighty GOD for giving me the capability, health and strength to complete the work
- Prof. D. de Waal (promoter) for her assistance, supervision and informed guidance. Thank you, also, for creating a conducive studying environment for me
- Annette Weitz and Monica van der Merwe for providing African clay pottery shards
- Prof. J. C. A. Boeyens for guidance and advice
- To the present and past research group members for the valuable discussions and advice
- Friends inside and outside the Department of Chemistry at UP for their invaluable advice and support
- My loving wife for her patience, encouragement and moral support
- NRF, Rolfes Pigments and University of Pretoria for the financial support

Summary

Raman spectroscopy is a vibrational spectroscopic technique. It gives a unique combination of non-destructive analysis, high spatial resolution and phase characterisation. In the current study Raman spectroscopy was used as the primary technique during the study of chemical components in archaeological earthenware samples (i.e. low temperature fired clay pottery) of South African and Chinese origin, and characterisation of iron oxides derived from mill scale.

One shard from each of the South African archaeological sites (Rooiwal, Lydenburg, Makahane and Graskop) was analysed by Raman spectroscopy, FT-IR spectroscopy, X-ray fluorescence (XRF) spectroscopy and X-ray diffractometry (XRD). The common features observed were montmorillonite ($\text{Mg}_3(\text{Si},\text{Al})_4(\text{OH})_2 \cdot 4.5\text{H}_2\text{O}[\text{Mg}]_{0.35}$), kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$), quartz ($\alpha\text{-SiO}_2$), feldspar (K- and $\text{NaAlSi}_3\text{O}_8$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), calcium silicate (CaSiO_3) and illite ($\text{KAl}_4(\text{Si}_7\text{AlO}_{20})(\text{OH})_4$). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium carbonates (CaCO_3) were detected in Lydenburg, Makahane and Graskop shards. Amorphous carbon was observed in Lydenburg and Makahane shards while rutile appeared only in Makahane shard. The Lydenburg and Rooiwal shards showed the presence of anhydrite (CaSO_4).

The Chinese clay samples investigated by Raman spectroscopy were from the J A Van Tilburg museum at the University of Pretoria. The large red shard was recovered from the 1552 Portuguese shipwreck, São João, found around Port Edward, South Africa. Four other shards (two red and two gray) were recovered from the 1622 Portuguese shipwreck, the São João Baptista, found around Kenton-on-Sea off the South African coast. A 19th century Chinese teapot was also analysed. Hematite, kaolin, quartz, amorphous carbon and aluminosilicates were observed in all three red shards. All these components, except quartz, were also observed in the teapot. The gray shards showed the presence of quartz, kaolin, amorphous carbon and aluminosilicates. The pigments identified were hematite (in red samples) and black amorphous carbon (in all samples).

Magnetite and goethite were precipitated from mill scale-derived precursors in aqueous media. Hematite was then prepared from the calcination of goethite at 750 °C and maghemite from the thermal treatment of magnetite at 200 °C. The iron oxides were characterised by Raman spectroscopy, XRD, surface area determination and scanning electron microscopy (SEM). They were generally composed of very small sized particles showing high surface area values.

Samevatting

Raman spektroskopie is 'n vibrasie spektroskopiese tegniek. Dit gee 'n unieke kombinasie van nievernietigende analise, hoë ruimtelike resolusie en fase karakterisering. In die huidige studie was Raman spektroskopie gebruik as die primêre tegniek vir die bestudering van chemiese komponente van argeologiese erdewerk monsters (m.a.w. lae temperatuur gevuurde erdewerk) van Suid-Afrikaanse en Chinese afkoms, en karakterisering van ysteroksiedes verkry van meulskaal.

Een skerf van elk van die Suid-Afrikaanse argeologiese terreine (Rooiwal, Lydenburg, Makahane en Graskop) was geanaliseer met Raman, X-straal fluoressensie (XRF), X-straal diffraksie (XRD) en FT-IR spektroskopie. Die algemeenste kenmerke was illite ($\text{KAl}_4(\text{Si}_7\text{AlO}_{20})(\text{OH})_4$), kaolien ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$), kwarts ($\alpha\text{-SiO}_2$), veldspaat (K- en $\text{NaAlSi}_3\text{O}_8$), hematiet ($\alpha\text{-Fe}_2\text{O}_3$), montmorilloniet $\text{Mg}_3(\text{Si,Al})_4(\text{OH})_2 \cdot 4.5\text{H}_2\text{O}[\text{Mg}]_{0.35}$, en kalsiumsilikaat (CaSiO_3). Gips ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) en kalsiumkarbonaat (CaCO_3) was waargeneem in die Lydenburg, Makahane en Graskop skerwe. Amorfe koolstof was waargeneem in die Lydenburg en Makahane skerwe, terwyl rutiel verskyn net in Makahane skerf. Die teenwoordigheid van anhidriet (CaSO_4) was ook waargeneem vir die Lydenburg en Rooiwal skerwe.

Die Chinese klei monsters wat vir Raman spektroskopie ondersoek gebruik was, was afkomstig uit die J A Van Tilburg museum van die Universiteit van Pretoria. Die groot rooi skerf was herwin van die São João, 'n 1552 Portugese skeepswrak, gevind naby Port Edward, Suid-Afrika. Vier ander skerwe (twee rooi en twee grys) was herwin van die São João Baptista, 'n Portugese wrak van 1622, gevind naby Kenton-on-sea, Suid-Afrika. 'n 19^{de} eeuse Chinese teepot was ook geanaliseer. Hematiet, kaolien, kwarts, amorfe koolstof en aluminosilikate was waargeneem in die teepot klei. Die grys skerwe het die teenwoordigheid van kwarts, kaolien, amorfe koolstof en aluminosilikate aangedui. Die pigmente wat geïdentifiseer is, was hematiet (in rooi monsters) en swart amorfe koolstof (in alle monsters).

Magnetiet en goethiet was gepresipiteer van meulskaal afkomstige voorgangers in waterige media. Hematiet was volgende voorberei deur goethiet te kalsineer by 750 °C. Maghemiet was voorberei deur die termiese behandeling van magnetiet by 200 °C. Al die ysteroksiedes was gekarakteriseer deur Raman spektroskopie, XRD, oppervlakte area bepaling en

aftaselektronmikroskopie (SEM). Die monsters was in die algemeen saamgestel uit baie klein partikels wat aanduidend is van hoë oppervlakte area waardes.

Table of contents

Declaration of oath	ii
Acknowledgements	iii
Summary	iv
Samevatting	vi
Table of contents	viii
Chapter 1	1
Overall introduction.....	1
1.1. Background	1
1.2. Rationale for the study.....	1
1.2.1. Earthenware objects.....	1
1.2.1.1. The standard procedure for making African clay pottery.....	2
1.2.1.2. The significance of chemical phases that constitute museum clay artefacts.....	3
1.2.2. Iron oxides.....	4
1.2.2.1. Theoretical background on inorganic pigments.....	5
1.2.2.2. Synthesis of iron oxides.....	7
1.2.3. Raman spectroscopy.....	9
1.3. Aims and objectives.....	9
1.4. Outline of the remaining chapters	10
1.5. References	11
Chapter 2	14
Literature review.....	14
2.1. Clay products	14
2.1.1. Origin of clays.....	14
2.1.2. Types of clay ceramics.....	15
2.1.3. Thermal evolution of clay minerals.....	15
2.1.4. Raman spectroscopic analysis of clay minerals.....	17
2.1.5. Conclusion.....	18

2.2. Synthesis of iron oxides	18
2.2.1. Red iron oxide (hematite, α -Fe ₂ O ₃).....	19
2.2.1.1. Synthesis using thermal methods.....	19
2.2.1.2. Synthesis using precipitation methods.....	20
2.2.2. Yellow iron oxide (goethite, α -FeOOH).....	21
2.2.2.1. Synthesis using precipitation methods.....	21
2.2.3. Brown iron oxide (maghemite, γ -Fe ₂ O ₃).....	22
2.2.3.1. Synthesis using thermal methods.....	22
2.2.3.2. Synthesis using precipitation methods.....	22
2.2.4. Black iron oxide (magnetite, Fe ₃ O ₄).....	23
2.2.4.1. Synthesis using thermal methods.....	23
2.2.4.2. Synthesis using precipitation methods.....	23
2.2.5. Conclusion.....	24
2.3. Raman spectroscopic analysis of iron oxides.....	25
2.4. References	27
Chapter 3	33
Raman spectroscopy	33
3.1. Theory of Raman scattering.....	33
3.2. Raman activity of vibration.....	35
3.3. Raman instrumentation	37
3.3.1. Light source.....	37
3.3.2. Optical system.....	38
3.3.3. Detector.....	39
3.4. Operational parameters	40
3.4.1. Laser power.....	40
3.4.2. Sample form.....	41
3.4.3. Sample recording time.....	42
3.4.4. Number of scan accumulations.....	42
3.4.5. Confocal microscope.....	42
3.5. References	43

Chapter 4	45
Raman spectroscopic study of ancient South African domestic clay pottery.....	45
Chapter 5	54
Raman analysis of red-brown and gray shards from 16th and 17th century Portuguese shipwrecks.....	54
Chapter 6	68
The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste	68
Chapter 7	79
Overall conclusion.....	79
7.1. Elemental analysis	79
7.1.1. X-ray fluorescence spectroscopy (XRF).....	80
7.1.2. Particle induced X-ray emission (PIXE).....	80
7.1.3. Laser induced breakdown spectroscopy (LIBS).....	81
7.1.4. Inductively coupled plasma (ICP).....	81
7.1.5. Neutron activation analysis (NAA).....	82
7.2. Chemical phase analysis	84
7.2.1. X-ray diffraction (XRD).....	84
7.2.2. Raman spectroscopy.....	85
7.3. Surface characterisation.....	85
7.3.1. Light microscopy.....	86
7.3.2. Scanning electron microscopy (SEM).....	86
7.3.3. Atomic force microscopy (AFM).....	87
7.4. Non-destructive testing	87
7.5. Application of Raman spectroscopy	88
7.5.1. Earthenware archaeological objects.....	88

7.5.2. Iron oxide pigments.....	89
7.5.3. Future work.....	91
7.6. References	92
Appendix	95