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

by

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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:……………….**

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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 ($Mg_3(Si,Al)_4(OH)_2.4.5H_2O[Mg]_{0.35}$), kaolin ($Al_2Si_2O_5(OH)_5$), quartz ($\alpha$-$SiO_2$), feldspar (K- and $NaAlSi_3O_8$), hematite (α-Fe_2O_3), calcium silicate ($CaSiO_3$) and illite ($KAl_4(Si_7AlO_{20})(OH)_4$). Gypsum ($CaSO_4.2H_2O$) 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 ^{o}C and maghemite from the thermal treatment of magnetite at 200 ^{o}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 spekroskopie 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 ($KaI_4(Si_7AlO_{20})(OH)_4$), kaolien ($Al_2Si_2O_5(OH)_5$), kwarts ($\alpha$-$SiO_2$), veldspaat (K- en $NaAlSi_3O_8$), hematiet (α-Fe_2O_3), montmorilloniet $Mg_3(Si,Al)_4(OH)_2{\cdot}4.5H_2O[Mg]_{0.35}$), en kalsiumsilikaat ($CaSiO_3$). Gips ($CaSO_4{\cdot}2H_2O$) 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 19de 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 ºC. Maghemiet was voorberei deur die termiese behandeling van magnetiet by 200 ºC. Al die ysteroksiedes was gekarakteriseer deur Raman spektroskopie, XRD, oppervlakte area bepalings en

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

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