Identification of Organic Pigments in Colored Pencils | 2000-26

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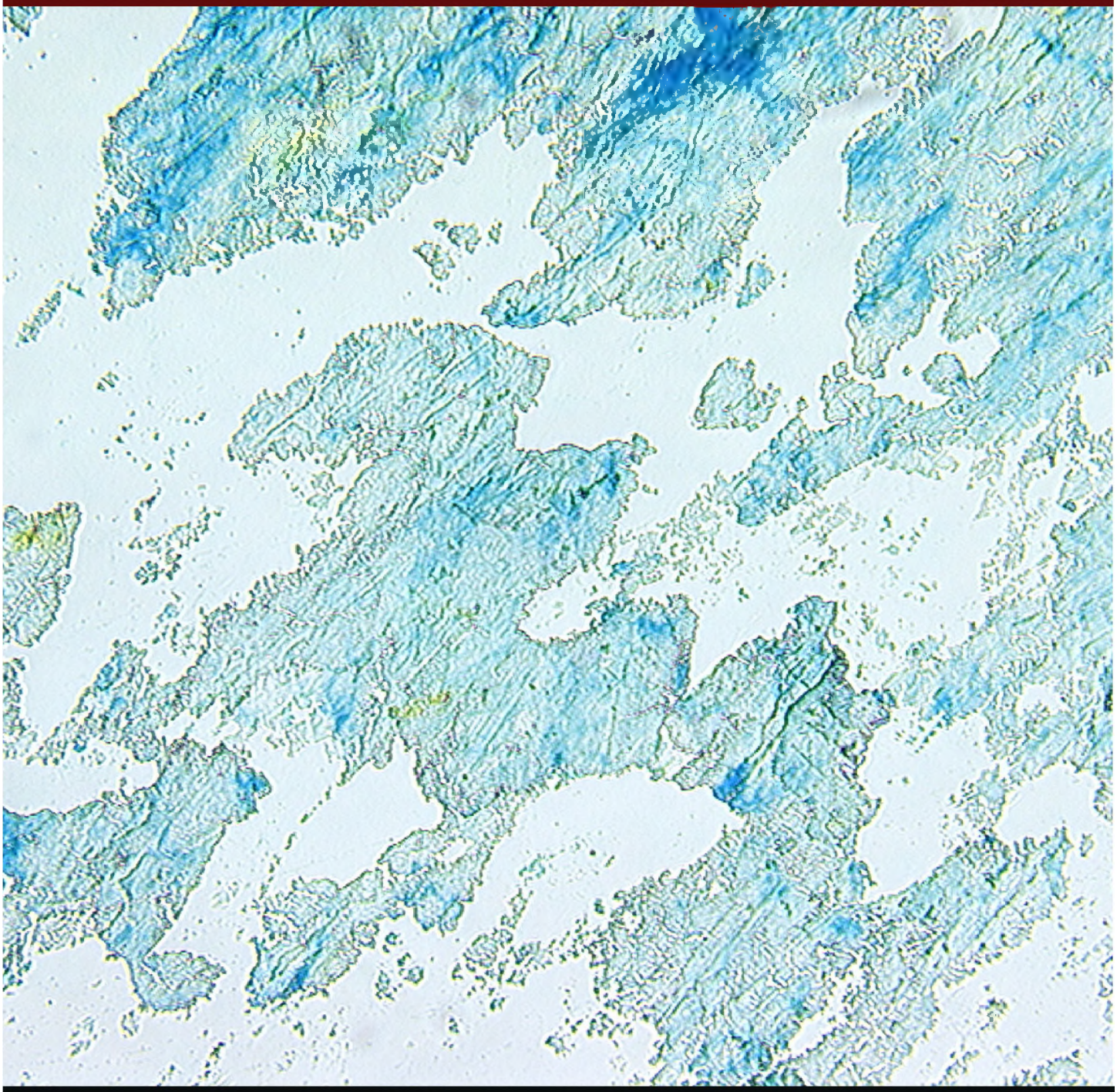

National Park Service
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FINAL REPORT

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)
INSTITUTE FOR STANDARDS RESEARCH (ISR) PROGRAM

PROJECT #9055

IDENTIFICATION OF ORGANIC PIGMENTS IN COLORED PENCILS

Date of completion: February 28, 2000

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CONTENTS

STATEMENT OF WORK

The stated objectives of this research project were to:

1) Refine an analytical test method that will successfully identify the organic pigments that exist in colored pencils.
2) Analyze, identify, and prepare a list of the organic pigments that exist in at least 300 colored pencils provided by suppliers.
3) Prepare and submit a scientific final report that provides a detailed summary of the work, the test method developed and used to prepare a list of pigments identified.

Potential Research Limitation

As described in the original project proposal and endorsed by ASTM D01.57, it was understood by the PI and the endorsers of the proposal that the success of the project in identifying all theorganic pigments that exist in the test pencils would depend on the following factors:

1) On the total number of organic pigments used in the manufacture of the pencils.
2) The transferability of Kumar's four-solvent separation system from paint binders to cobred pencil leads.
3) The commercial availability of representative reference spectra for solution spectrophometry and FT-IR.

Due to these unknown variables, neither the PI nor ISR could guarantee that all organic pigments will be identified. The research however, despite this potential limitation, was performed in good faith with every intention of meeting the deliverable as proposed.

Timeframe for Completion

The proposal called for completion of work and submission of the final report at the end of fourteen (14) months from date of contract award to PI and ISR from: August 28, 1998 to October 28, 1999. An extension was requested and received September 29, 1999 to permit additional testing from October 28, 1999 to February 28, 2000.

DETAILED SUMMARY OF WORK

SAMPLE DESCRIPTION

Three hundred twelve (312) colored pencils were provided from each of six manufacturers representing the most widely used brands marketed as fine art materials. The pencils were blinded (stripped of identifying commercial information), coded, and sent to the Principal Investigator (PI) by Joy Turner Luke and Rhonda Farfan, who assigned codes to the test pencils: LB 01-52, LA 53-104, RC 106-157, RD 158-209, RE 210-261, and RF 262-313. The manufacturers' identities were not reported to the PI, per the terms of the contract.

TEST PROTOCOL USED IN THE ANALYSIS

Specimen collection

Specimens of each pencil lead were obtained from the bulk pencils for analysis. Advantage was taken of the previously sharpened, but blunt, tip of each pencil. Possible contamination from other pencils, accumulated debris, and unknown chemical alteration of the exposed lead surface was removed by rubbing the tip, while twisting, across clean, white copy paper.

Two sets of specimens were removed for examination and analysis. Particle specimens for optical microscopy were removed using clean #11 steel scalpel blades. The amount of material removed was estimated to be in the microgram (µm) range. These specimens were transferred to clean, glass microscope slides, where they were dispersed for examination using a Spectra-Tech steel roller.

Powder specimens for solvent extraction were removed using clean, single-edge razorblades. Approximately 40-50 milligrams (mg) of each pencil lead was scraped directly into a 4-milliliter (ml) glass vial labeled 'insoluble' and marked with the related alphanumeric pencil code.

Solvent extractions

Solvent extractions were made using Omnisolv HPLC/spectrophotometric grade solvents. The solvents, in order of use, were hexanes, chloroform, methanol, and N,N-dimethyl formamide. Kumar's four-solvent system included chloroform, methanol, N,N-dimethyl formamide, and sulfuric acid. The substitution of hexane for sulfuric acid was made to remove the wax binder. All extractions were made in-situ in the "insoluble" vial. Hence, with 312 pencil samples, over 1500 vials were produced.

Hexane extraction. In order to remove the wax binder – identified in preliminary analyses of neat pencil leads – and other non-polar materials, 3.5 ml of hexane was added by glass Pasteur pipette to the vial. The vial was sealed with a fluid-tight cap and its contents were sonicated to insure thorough disaggregation of the sample, thereby maximizing surface contact between sample and solvent to maximize the extraction yield. The vial was then centrifuged to settle insoluble or undissolved particles suspended in the solution. The hexane fraction was transferred by pipette to a vial labeled "Hex". The open "insoluble" vial was heated for approximately 10 minutes in a 50C oven to evaporate any residual hexane.

Chloroform, methanol, and N,N-dimethyl formamide (DMF) extractions. The same procedure was followed for extractions of organic pigments using chloroform, methanol, and N,N-dimethyl formamide. Each solute was transferred to a vial labeled "$CHCl_3$", "MeOH", or "DMF," respectively. In many cases, a brightly colored solution was obtained, indicating successful isolation of increasingly polar pigments across the spectrum of solvents employed.

Solution spectrophotometry

Solution spectrophotometry was the first analytical technique employed in the project. Analyses were made using a Hewlett Packard 8452A diode array spectrophotometer and a Hewlett Packard PC running 85391A software. Please see Appendix B for printed spectra.

Approximately 700 spectra were collected of colored solutions in chloroform, methanol, and N,N-dimethyl formamide. Spectra were collected in log absorbance (1/absorbance) units from 380 to 820 nanometers (nm) at 2 nm resolution. Samples were analyzed in quartz cuvettes (1 ml volume, 1.00 centimeter path length), and were diluted with additional solvent as required to maintain absorbance values between 0.9 and 1.2. Spectral reproducibility was monitored using a phendphthalein standard; no problems were observed during data collection. Cuvettes were double rinsed with fresh solvent between uses; no cross-contamination by improper cleaning was observed.

Spectra were not used for identification, because of the absence of commercially available UV/VIS spectral libraries, and the non-uniformity of Kumar's original UV-VIS data (provided by Ms. Luke). The spectra, however, were compared to complement FTIR analyses.

Comparison of spectra was made using commercial software: Grams32 (version 5.10) with Grams Spectral ID (version 1.01). Searchable user libraries were created for each manufacturer-solvent combination (e.g., group LA-chloroform), resulting in 18 libraries. Spectra were grouped and compared by solvent, because each solvent gave a different spectrum for a given pigment. Each sample spectrum was added to its corresponding library. Spectra were grouped and compared by manufacturer to streamline comparison.

Actual comparison was made in two steps, as follows. 1) The Spectral ID software was employed make rapid and reproducible association between samples within each manufacturer-solvent group. The software search algorithm did this by comparing data points in the sample spectra with data points in all library spectra. Each spectrum was searched against spectra in its group. Associations were presented in decreasing order of similarity, by match index. A perfect match would give a match index of 100. 2) Visual comparison of sample and top match spectra was made to gain a qualitative sense for the degree to which secondary or minor pigments were present in a sample. When necessary, spectral subtraction techniques proved useful in discriminating minor components of a solution containing two or more pigments.

Note. It is important to note that all of the assignments were based on grouping common spectra and not by employing a reference library of known standards, as was done with the FTIR analysis. After association groupings were made, the UV/VIS and FTIR assignments were compared and names were given to the UV/VIS groupings based on their agreement with the FTIR data. Overall, the UV/VIS analysis proved to be in excellent agreement with the FTIR analysis, although it was not as complete and accurate as FTIR.

Fourier transform infrared microspectroscopy (FTIR)

FTIR was the second technique employed in the project. Analyses were made using a SpectraTech Research IRPlan microscope coupled to a Nicolet Magna 550 FTIR bench– both purged with clean, dry air. All analyses were made in transmission mode, on a diamond window, using 15x or 32x reflachromat objectives. Fixed circular or variable rectangular redundant apertures were used to mask an area for analysis. The aperture diameter was maximized for signal-to-noise; typical areas ranged from 50-100 microns. A spectral range of 4000 to 650 wavenumbers (cm^{-1}) was analyzed using a nitrogen-cooled MCT-A detector in the microscope. Thirty-two (32) or more sample and background scans were collected at 4 cm^{-1} resolution. Data was plotted and analyzed using Nicolet OMNIC ESP (4.1.a) software. Please see Appendix A for printed spectra.

FTIR spectra of solvent extractions would show the solvent, in addition to dissolved organic pigments. For this reason, solvent was removed from extract specimens before analysis. Removal was made using two procedures, which are described below. (Hexane fractions were set aside because none contained enough colored material to visually indicate the presence of a soluble pigment.)

Droplets of the colored solutions in chloroform, methanol and DMF were spotted onto clean glass slides. The slides initially were warmed to concentrate the size of the spots. Residual solvent was evaporated at room temperature. FTIR spectra of these dried specimens were superior for pigment

identification to those obtained from preliminary analyses of neat leads. However, many spectra revealed non-pigment material (wax, clay, unknown additives) that obscured portions of the spectrum and complicated spectral searching and identification. For this reason, a second procedure was used that provided purer specimens for analysis.

Following analysis by solution spectrophotometry, solvent in the colored extract vials was allowed to evaporate slowly over a period of several months, at room temperature. This process allowed organic pigments to recrystallize from solution. In many cases, this procedure yielded superior specimens for FTIR analysis – chemically pure crystals showing distinctive form and color that were sufficiently large to be physically separated, even in samples containing two or more pigments.

Sample spectra were interpreted for content by visual inspection of peak position and intensity. Peak positions were identified using the peak find tool in OMNIC. Possible identifications were aided using software search algorithms provided in OMNIC. The correlation algorithm was used in each case. The full spectral region was used for sample spectra that did not evidence clay, wax, or other additives. A partial spectral region, from about 1800 to 1200 cm^{-1} was used for sample spectra containing clay and wax. The following libraries were used for spectral search:

- Aldrich Dyes, Indicators, Nitro and Azo Compounds
- Commercial Materials Painter Minerals
- Coatings Technology (high resolution)
- Hummel Polymer and Additives (high-resolution)
- Polymer Additives and Plasticizers (high-resolution)
- U.S. Geological Survey Minerals
- Infrared Users Group (IrUG) Pigments and Dyes (high-resolution)
- Raw pigments provided by Kremer Pigments, Magruder Color Company, and Sun Chemical (in-house, high-resolution)

Identification was made by direct visual comparison of sample and reference spectra. When spectra were comparable, but identification could not be made, the spectrum was said to "indicate" or "suggest" a specific material or class of material.

Qualitative energy-dispersive x-ray fluorescence spectrometry with the scanning electron microscope (SEM-EDS)

Qualitative SEM-EDS was used to determine the elemental composition of insoluble fractions and to confirm the composition of pencil specimens representative of identified pigments. Analyses were made using a Cambridge Stereoscan 100 scanning electron microscope equipped with a

Tracor/Northern energy-dispersive spectrometer. Please see Appendix C for a summary of SEM-EDS results.

With the aid of a stereomicroscope, representative particles were taken directly from the insoluble vials, and compressed into a thin sheet on a clean glass slide with a stainlesssteel roller. The rolled samples were then transferred to an aluminum stub with carbon adhesive tape and made conductive with a thin coating of carbon.

Energy-dispersive x-ray spectra were collected using a Tracor/Northern energy-dispersive spectrometer and a TN5500 analyzer. Data was collected at a standard working distance of 40 mm, aspect angle of 30 degrees, and accelerating voltage of 25 kV. Collection times were sufficiently long to clearly discern the presence of trace elements (approximately one minute). The system is sensitive to about 5% by weight, and elements that have an atomic number of 11 (sodium) and greater.

Elemental identification was made by direct visual inspection of x-ray spectra. Identifications were confirmed using automated peak identification software. Pathological overlap of x-ray energies can make it difficult, or impossible, to differentiate the presence or absence of these elements, especially when present in low concentration or mixtures.

Optical microscopy

Optical microscopy was used to evaluate the homogeneity of samples, based on the color and fluorescence of component particles. Examinations were made using an Olympus BX60 polarizing light microscope equipped for Koehler illumination, and fitted 4x, 10x, 20x,40x, and 100x fluorite (semi-apochromat) objectives, and ultraviolet and blue-violet excitation/emission filters.

Samples were inspected by eye using transmitted and reflected polarized light, and reflected fluorescence illumination. Digital images of transmitted, plane-polarized views were collected using a Sony DKC-5000 (Catseye) digital camera system, and printed using a Sony 1500 digital dye sublimation printer. Please see Appendix D for digital images (3 CD-ROM disks).

RESULTS

PIGMENTS IDENTIFIED

The following table lists pigments identified by FTIR. ASTM nomenclature is used where applicable. The first three columns give the Color Index Name, Pigment Name, and Color Index Number, respectively. The last six columns show the number of times each pigment was identified in each manufacturer group.

CI name	Pigment name	CI #	LA	LB	RC	RD	RE	RF
PB001	Victoria blue	42595	1	4	1		1	8
PB015	Phthalocyanine blue	74160	10	12	16	16	12	9
PB027	Prussian Blue **(not organic)**	77510		2				4
PB060	Indanthranone blue	69800			4			
PG007	Phthalocyanine green	74260	4	3	7	5	4	1
PO013	Pyrazolone orange	21110	2	10	3		3	
PO016	Dianisidine orange	21160				4		
PO016/PO005	Dianisidine or DNA orange (reference spectra are uncertain)							4
PO034	Tolyl Orange (diarylide)	21115	2				1	
PO036	Benzimidazalone Orange (azo)	11780				1		
PR003	Toluidine Red (azo)	12120	1			1	1	
PR004	Parachlor Red (azo)	12085		2	2		1	7
PR009	Naphthol Red AS-OL (azo)	12460	1		2		1	
PR022	Naphthol Red AS (azo)	12315			2			
PR023	Naphthol Red (azo)	12355			2			
PR048	2B reds (Ca, Mn, and Na salts) (azo)	15865		18	2	6		6
PR057	Lithol Rubine (Na, Ca salts) (azo)	15850				3		
PR081	Rhodamine Y	45160	5	5	1	2	2	10
PR112	Naphthol Red AS-D (azo)	12370	4	5	4	13	5	
PR122	Dimethyl Quinacridone	73915	2		3	1		
PR146	Naphthol Carmine FBB (Azo)	12485	1				2	
PR168	Brominated anthraquinone	59300			2			
PR170	Naphthol Red (azo)	12475	4				4	8
PR202	Dichloro Quinacridone (magenta b)	73907			4			
PR209	Dichloro Quinacridone (red y)	73905			2		1	

CI name	Pigment name	CI #	LA	LB	RC	RD	RE	RF
PV001	Rhodamine B	45170	3	10	1	2	3	5
PV003	Methyl violet	42535	1			2	2	1
PV016	Manganese violet (pyrophosphate) – **inorganic**	77742	1			5	2	
PV019	Quinacridone (unsubstituted)	73900	2		4	5	1	
PV023	Carbazole (dioxazine)	51319	3	2	4	2	2	
PY001	Hansa Yellow G (monoarylide)	11680	5	6	3	2	7	9
PY003	Hansa Yellow 10g (monoarylide)	11710	5	2	5		6	6
PY013	Diarylide Yellow AAMX	21100	1	5	1		1	
PY074	Arylide Yellow (monoarylide)	11741	2				6	1
PY083	Diarylide Yellow HR	21108			1		1	

PIGMENTS DETECTED BUT NOT IDENTIFIED

The following table lists pigments that have been detected, but not yet identified. Matches for these FTIR sample spectra were not found in any of the commercial or in-house libraries used, including the more extensive database of spectral libraries at the Nicolet Instrument Corporation. The first column lists a pencil extraction in which the pigment was detected (c: chloroform, m: methanol, d: N,N-dimethyl formamide). The second column lists the pigment description (color and present best guess of composition). The last six columns show the number of times each pigment was identified in each manufacturer group.

Pencil code	Pigment description	LA	LB	RC	RD	RE	RF
149d	Unidentified yellow (contains chlorine)			1			
195m	Unidentified red/violet (naphthol suggested)				3		
210d	Unidentified red (possible benzimadazalone)	1		3		1	
222d	Unidentified red (naphthol suggested)	1				1	
261c	Unidentified red/orange (naphthol suggested)	2					

SUMMARY OF RESULTS BY PENCIL

The following table provides more comprehensive FTIR, UV/VIS, and SEM-EDS data for each pencil. Pencils are listed by their alpha-numeric code and color in visible light. "IR Assignments" indicate pigments detected by FTIR, listed by Color Index name. "UV/VIS assignments" indicate pigments detected by UV/VIS solution spectrophotometry, listed by Color Index name. No organic

pigments were identified in twenty-one (21) pencils. The reason for no identification may be the absence of organic pigments, the presence of organic pigments below detection limits, and/or the use of inorganic pigments. UV/VIS listings for PR081/PV001 and PY001/PY003 indicate that one or both of the pigments were indicated, but could not be differentiated by the technique.

"EDS assignments" indicate elements detected at levels above typical levels for the given manufacturer. "TiO2/SiO2" shows a normalized (unitless) value for the relative amount of titanium in the insoluble fraction for each pencil, determined as a ratio of the primary peak area for titanium to the primary peak area for silicon. Please see the Appendices for more information about each set of data.

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
LB001	purple	PV001, PR048:2	PR081/PV001, PR048	Fe	0.14
LB002	red-purple	PV001, PR048:2	PR081/PV001, PR048	--	0.45
LB003	red-purple	PV001, PR048:2	PR081/PV001, PR048	--	0.11
LB004	Red	PV001, PR048:4	PV001, PR048	--	0.03
LB005	orange	PR112, PY013	PR112, PY003/PY001	--	0.50
LB006	orange	PO013	PO013	--	0.01
LB007	orange	PR004, PO013	PR004	--	0.06
LB008	orange	PR004	PR004	--	0.02
LB009	yellow	PY013	PR048	--	0.01
LB010	red	PR048:2	PR048	--	0.15
LB011	red	PO013, PR048:4, PR048:2	PO013, PR048	--	0.03
LB012	red	PO013, PR048:4, PR048:2	PO013, PR048	--	0.19
LB013	red	PR112	PR112	--	0.01
LB014	red	PY003, PR048:4, PR048:2	PY003/PY001, PR048	--	0.06
LB015	pink	PR048:2, PO013	PO013, PR048	--	0.61
LB016	pink	PR081, PV001, PR048:2	PR081/PV001, PR048	--	0.38
LB017	purple	PR081, PV001, PR048:2	PR081/PV001, PR048	--	0.14
LB018	red	PR048:2	--	--	0.02
LB019	violet	PR048:2	PR048	--	0.12
LB020	orange	PR048:4, PR048:2, PY013	PR048, PY013	--	0.36
LB021	violet	PV001, PR048:2	PR048	Fe	0.00
LB022	purple	PV023	PR081/PV001	--	0.37
LB023	purple	PR081, PV001	PR081/PV001	--	0.12
LB024	pink	PR048:2	--	--	0.63
LB025	pink	--	PR081/PV001	--	0.25

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
LB026	Peach	PR112, PY001	PR112	--	0.50
LB027	Purple	PV001, PR081, PB015	PR081/PV001	--	0.21
LB028	red-violet	PR048:2	PR048	Fe	0.00
LB029	dark blue	PB015	--	--	0.45
LB030	light blue	PB015	--	--	1.37
LB031	light blue	PB001	PB001	--	0.86
LB032	dark blue	PB001, PB027	PB001	Cu	0.12
LB033	blue	PB015	--	--	0.29
LB034	purple	PV001, PR081, PB015	PR081/PV001	--	0.20
LB035	blue	PY001, PB015	PY003/PY001	--	0.86
LB036	dark blue	PB015	--	Cu	0.13
LB037	dark blue	PB015, PV023	--	Cu	0.15
LB038	green	PY001, PB015	PY003/PY001	--	0.33
LB039	light blue	PB001	PB001	--	0.45
LB040	green	PG007	--	--	0.55
LB041	blue-green	PB015, PG007	PB015	--	0.40
LB042	dark blue	PB001, PB027	PB001	Fe, Cu	0.03
LB043	green-blue	PY003, PB015	PY003/PY001, PB015	Cu	0.35
LB044	yellow	PY013	--	--	0.61
LB045	pink	PY001	PY003/PY001	--	0.39
LB046	light purple	--	--	--	0.38
LB047	peach	PR112, PO013	--	--	0.53
LB048	dark orange	PO013	PO013	--	0.02
LB049	yellow	PY001	PY003/PY001	--	0.08
LB050	orange	PR112, PO013	PO013	--	0.05
LB051	light orange	PO013, PR048:2	PO013, PR048	--	0.63
LB052	green	PY001, PG007	--	--	0.47
LA053	yellow	PY003	PY003/PY001	--	0.00
LA054	yellow	PY001, PY003	PY003/PY001	--	0.00
LA055	yellow	PY074	PY074	Fe	0.68
LA056	yellow	PY013	PY013	--	0.00
LA057	orange	PY001, PO034	PY003/PY001	--	0.00
LA058	blue	PB015	PB015U	--	0.06
LA059	orange	PO013, U 210d	PO013, U 210d	--	0.30
LA060	orange	PO013	PO013	--	0.34

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
LA061	orange	PO034	PO034	--	0.00
LA062	orange	--	--	--	0.00
LA063	red-orange	PR003	PR003	--	0.00
LA064	light purple	PR122	--	--	0.25
LA065	blue	--	--	--	0.00
LA066	red	PR112	PR112	--	0.00
LA067	violet-red	PV019	PV019	--	0.24
LA068	pink	PR112, PR170	PR112, PR170	Fe	0.74
LA069	red-violet	PR122	PR122	--	0.18
LA070	red	PR112	PR112	--	0.00
LA071	red	PV019, PR170	PR112	--	0.25
LA072	pink	PR081	PR081	--	0.33
LA073	pink	UNIDENTIFIED INSOLUBLE	PR209	--	0.73
LA074	pink	PR009	PR009	Fe	1.24
LA075	pink	PY003, U 222d	PY003/PY001	Fe	0.65
LA076	pink	PY003	PY003/PY001	Fe	0.66
LA077	red-violet	PV001, PR081, U 261c	U 261c, PVOO1, PR081	--	0.00
LA078	purple	PR081, PV001	PV001, PR081	--	0.17
LA079	light violet	PR081, PR170, PV016	PR170	Mn, P	0.06
LA080	purple	PV001, PR081	PR081/PV001	--	0.15
LA081	purple	PV003	PV003	--	0.14
LA082	light purple	PV023	--	--	0.58
LA083	light purple	PV023	--	--	0.23
LA084	blue	--	--	--	0.12
LA085	purple	PV023, PB015	PV023	--	0.24
LA086	blue	PB001	PB001	--	0.19
LA087	blue	PB015	PB015	Cu	0.83
LA088	light blue	PB015	PB015	Cu	0.37
LA089	light blue	--	--	Zn	0.73
LA090	light blue	--	--	--	0.25
LA091	green-blue	PB015	PB015	Cu, Cl	0.13
LA092	blue	PB015	PB015	Cu, Cl	0.00
LA093	blue	PB015	PB015	--	0.22
LA094	blue-green	PB015, PG007	PB015, PG007	Cu, Cl	0.00
LA095	light blue	PB015, PG007	PB015	--	0.23

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
LA096	blue-green	PY001, PB015	PY003/PY001, PB015U	Cu, Cl	0.00
LA097	green	PG007	PG007	--	0.59
LA098	green	PY001, PG007	PY003/PY001, PG007	--	0.21
LA099	green	PY001, PY003	PY003/PY001	--	0.00
LA100	yellow	PY074	PY074	Fe	0.48
LA101	dark peach	PR112	--	Fe	0.00
LA102	brown	PR146	PR146	Fe	0.00
LA103	red-brown	PR170	PR112, PR170	Fe	0.00
LA104	violet-brown	U 261c	U 261c, PR170	Fe	0.00
RC106	yellow	PY083	--	--	1.27
RC107	orange	PO013, PY013	PO013, PY013	--	0.20
RC108	orange	PR112, U 210d	PR112, U 210d	--	0.22
RC109	orange	PY001, PR009, U 210d	PY003/PY001	--	0.27
RC110	orange	U 210d, PR168	U 210d	--	0.22
RC111	red	PR004	PR004	--	0.23
RC112	red	PR009	--	Fe	0.07
RC113	pink	PR004	PR004	--	0.16
RC114	pink	PR112, PR168	PR022	--	1.14
RC115	red	PR112, PR023	PR112	--	0.61
RC116	violet	PR023	PR112, U 210d	--	0.30
RC117	pink	PV019	PR048, PV019	--	0.92
RC118	pink	UNIDENTIFIED INSOLUBLE	--	--	0.97
RC119	violet	PR112, PR048:4, PR048:2, PV019	PR112, PR048	--	0.51
RC120	violet	PR048:4, PR048:2	PR048	--	0.37
RC121	purple	PR202	PR202	--	0.39
RC122	pink	PV019	PV019	--	0.41
RC123	purple	PR202	--	--	0.81
RC124	purple	PV019	--	--	0.53
RC125	purple	PR122	PR122	--	0.55
RC126	purple	PV001, PR081, PR122	PR081/PV001, PR122	--	0.72
RC127	purple	PR122, PV023	PV003, PR122, PV023	--	0.47
RC128	purple	PV023, PB015	--	--	0.33
RC129	purple	PV023	--	--	0.19
RC130	blue	PV023, PB015	PV023	--	0.24
RC131	blue	PB015	PB015	Cu, Cl	0.28

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
RC132	blue	PB015	--	--	0.92
RC133	blue	PB060	--	--	0.32
RC134	blue	PB015, PR202, PB060	PB015, PR202	--	0.43
RC135	blue	PB015	PB015	Cu	0.22
RC136	blue	PB015, PB060	--	--	0.92
RC137	blue	PB060	PB015	--	0.72
RC138	blue	PB001, PG007	PB001	--	0.13
RC139	blue	PB015, PG007	PB015	Cu, Cl	0.42
RC140	blue	PB015	PB015	--	0.63
RC141	blue	PB015	PB015	Cu	0.20
RC142	green	PB015, PG007	PG007, PB015	Cu, Cl	0.48
RC143	blue	PB015, PG007	PB015	--	0.61
RC144	green	PG007	--	--	1.18
RC145	green	PY001, PY003, PG007	PY003/PY001	--	0.36
RC146	green	PY003	PY003/PY001	--	2.14
RC147	green	PO013, PY003, PB015	PY003/PY001	--	0.63
RC148	green	PO013, PY003	PY003/PY001	--	0.43
RC149	yellow	U 149d	U 149d	--	0.31
RC150	blue	PB015	--	Cu	0.28
RC151	pink	PR209	PR209	--	0.23
RC152	red	PR022	PR009, PR022	--	0.16
RC153	violet	PR209, PR202	PV209	--	0.23
RC154	blue	PB015	PB015	Cu	0.22
RC155	blue	--	--	--	1.30
RC156	green	PY003	PY003/PY001	--	0.21
RC157	peach	--	--	--	0.73
RD158	orange	PR112, PO016	PO016	--	0.22
RD159	orange	PR112, PO016	PO016	--	0.20
RD160	orange	PR112, PO016	PO016	--	0.38
RD161	red	PR112, PY001	PR112, PY003/PY001	--	0.43
RD162	red	PR003	PR003	--	0.00
RD163	pink	PR112	PR112	--	0.35
RD164	pink	--	--	Mn, P	0.41
RD165	pink	PR112, PO016	PO016, PR112	--	1.09
RD166	pink	PR112	PR112	--	0.34

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
RD167	violet	PR112, PR048:4	PR112, PR048	Fe	0.02
RD168	violet	PR112, PR048:2, PR048:4	PR112, PR048	--	0.31
RD169	violet	PR048:4, PR048:2	PR048	--	0.00
RD170	violet	PR048:4	PR048	Fe	0.42
RD171	violet	PR112	PR112, PV001	--	0.30
RD172	violet	PR048:4, PR048:2	PR048	--	1.02
RD173	purple	PR048:4, PV023	PR048, PV023	--	0.40
RD174	purple	PV001, PR081	PR081/PV001	--	0.27
RD175	purple	PV016	--	Mn, P	0.47
RD176	purple	PV016	--	Mn, P	0.37
RD177	purple	PV001, PR057:1, PR081, PB015	PR081/PV001	--	0.15
RD178	purple	U 195m, PV019, PR122	U 195m, PB019	--	0.10
RD179	purple	PV016	--	Mn, P	0.28
RD180	purple	PR057:1, PV003, PB015	PV001/PR081, PV003	--	0.24
RD181	purple	PV019	PV019	--	0.84
RD182	blue	PV019, PB015	PV019	--	0.43
RD183	blue	U 195m, PB015, PV023	U 195m, PB015	--	0.23
RD184	blue	PV016	--	Mn, P	0.00
RD185	blue	--	--	--	0.23
RD186	blue	PV016	--	Mn, P	0.86
RD187	blue	--	--	--	0.47
RD188	blue	PV003, PB015	PV003A	--	0.25
RD189	blue	PV019, PB015	PV019	--	0.40
RD190	blue	PV019, PB015	PV019	--	0.52
RD191	blue	PB015	PB015	--	0.28
RD192	blue	PB015	PB015	--	0.19
RD193	blue	PB015	--	--	0.67
RD194	blue	PR057:1, PB015	PR048, PB015	--	0.32
RD195	blue	U 195m, PB015	U 195m, PB015	Cu	0.07
RD196	blue	--	--	--	0.35
RD197	blue	PB015	PB015	Cu	0.19
RD198	blue	PB015	PB015	--	0.74
RD199	blue	PB015, PG007	PB015	Fe?, Cu, Cl	0.38
RD200	blue	PB015, PG007	PB015	--	0.24
RD201	blue	PG007	--	--	0.76

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
RD202	green	PG007	PG007	--	0.23
RD203	green	PY001, PG007	PY003/PY001	--	0.25
RD204	orange	PO036	PO036	Fe?	0.41
RD205	red	PR112	PR112	Fe	0.36
RD206	peach	--	--	Fe	0.38
RD207	red	PR112	PR112	Fe	0.33
RD208	violet	PV016	--	Fe, Mn, P	0.45
RD209	violet	PR112	PR112	Fe	0.38
RE210	orange	U 210d	--	--	0.29
RE211	orange	PO013	PO013	--	0.28
RE212	orange	PO034	PO013, PO034	--	0.26
RE213	orange	PR004	PR004	--	0.00
RE214	red	PR003	PR003	--	0.00
RE215	red	PR112	PR112	--	0.00
RE216	pink	PR112, PR170	PR112	Fe	0.60
RE217	violet	PR112	PR112	--	0.00
RE218	violet	PR170, PV019	PV019	--	0.30
RE219	pink	PR081	PR081	--	0.22
RE220	pink	PR209	PR209	--	0.65
RE221	pink	PR009	PR009	Fe?	0.67
RE222	pink	PY003, U 222d	PY003/PY001	Fe?	0.55
RE223	peach	PY003	PY003/PY001	Fe?	0.65
RE224	purple	PV001, PR081	PV001, PR081, PR112	--	0.00
RE225	purple	PV001	PR081/PV001	--	0.20
RE226	purple	PR170, PV016	PR170	Mn, P	0.08
RE227	purple	PV001, PV003	PR081/PV001	--	0.19
RE228	purple	PV003	PV003	--	0.13
RE229	purple	PR146, PV023	PR146	--	0.50
RE230	purple	--	--	--	0.10
RE231	purple	PV023	PV023	--	0.26
RE232	blue	PB001	PB001	--	0.14
RE233	blue	PB015	PB015	Cu	0.73
RE234	blue	UNIDENTIFIED INSOLUBLE	--	Zn	0.76
RE235	blue	--	--	--	0.62
RE236	blue	PB015	PB015	--	0.68

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
RE237	blue	PB015	PB015	Cu, Cl	0.00
RE238	blue	PB015	PB015	Cu	0.37
RE239	blue	PB015	PB015	Cu, Cl	0.00
RE240	blue	PB015, PG007	PB015, PG007	Cu, Cl	0.14
RE241	blue	--	--	--	0.22
RE242	green	PY001, PB015	PY003/PY001, PB015	Cu, Cl	0.00
RE243	green	PY074, PB015, PY003	PY003/PY001, PB015	Cu	0.00
RE244	green	PY001, PY003, PB015	PY003/PY001, PB015	Cu	0.00
RE245	green	PY001, PG007	PY003/PY001, PG007	Cu, Cl	0.16
RE246	green	PY003, PG007	PY003/PY001, PG007	Cu, Cl	0.13
RE247	green	PY001, PB015	PY003/PY001, PB015	Cu	0.00
RE248	green	PY013	--	--	0.21
RE249	green	PY074	PY074	--	0.00
RE250	green	PY074, PB015	PY074	--	0.00
RE251	green	PY001, PY003, PG007	PY003/PY001	--	0.00
RE252	green	PY074	PY074	Fe?	0.29
RE253	green	PY074, PY083	--	--	0.31
RE254	green	PY001, PB015	PY003/PY001, PB015	--	0.26
RE255	brown	PO013, PY001	PY003/PY001	Fe	0.00
RE256	yellow	PY074, PO013	PY074	Fe?	0.00
RE257	red	PR112	PR112	Fe	0.00
RE258	red	PR112	PR112	Fe	0.00
RE259	violet	PR146	PR146, PR004	Fe	0.00
RE260	violet	PR170	PR112, PR170	Fe	0.00
RE261	violet	U 261c	U 261c, PB001	Fe	0.00
RF262	blue	PB027	PB027	Fe	0.03
RF263	blue	PB001	PB001	--	1.64
RF264	blue	PB015	PB015	Cu	1.85
RF265	blue	PB001	--	--	2.11
RF266	blue	PY003, PG007, PB015	--	Cu	1.88
RF267	blue	PY003, PB001, PB015	PB015, PB001	Cu	1.13
RF268	green	PY003, PB001, PB015	PY003/PY001, PB001	Cu	0.24
RF269	orange	PO005/16	PO005/16	--	1.52
RF270	blue	PB015	--	--	2.12

Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
RF271	orange	PR004, PR048:2	PR004	--	1.81
RF272	red	PY074, PY001, PR048:2	PY003/PY001, PY074, PR048	--	0.76
RF273	red	PY001, PY003, PR170	PY003/PY001	--	0.24
RF274	red	PR170, PO005/16	PO013, PR170	--	0.05
RF275	pink	PR004, PR048:2	PR004	--	1.59
RF276	pink	PR004, PR081, PV001, PR048:2	PR004, PR081	--	2.86
RF277	violet	PR081, PR170	PR081	--	1.48
RF278	purple	PV001, PR081	PV001/PR081	--	0.04
RF279	purple	PV001, PR081, PB015	PR081/PV001	--	2.34
RF280	blue	PB001	PB001	--	0.53
RF281	pink	--	PV001	--	2.33
RF282	gray	PB027	PB001	Fe	3.19
RF283	brown	PY001, PR170	PY003/PY001, PR170	Fe	0.05
RF284	peach	PR004	PR004	Fe	2.96
RF285	purple	--	PR081/PV001	--	2.05
RF286	green	PY001, PR004, PB027	PY003/PY001	--	2.21
RF287	blue	--	--	--	1.39
RF288	pink	PR081	PR081	--	1.60
RF289	pink	PR081	PR081	--	3.80
RF290	violet	PR081	PR081	--	1.90
RF291	purple	PR170, PB015	PR170	--	2.16
RF292	orange	PY001, PR004	PY003/PY001	--	1.95
RF293	green	PY001, PY003	PY003/PY001	--	0.91
RF294	green	PY001, PY003	PY003/PY001	--	0.37
RF295	purple	PB001, PV003	PB001, PV003	--	1.69
RF296	purple	PV001, PR081	PR081/PV001	--	2.99
RF297	violet	PV001, PR081	PR081/PV001	--	0.29
RF298	blue	--	--	--	1.92
RF299	violet	PR048:2	PR048	Fe	2.68
RF300	pink	--	--	--	2.69
RF301	violet	PR048:2	PR048	Fe	4.13
RF302	blue	--	PV019	--	1.63
RF303	blue	PB027	PB027	Fe	2.58
RF304	blue	PB001	PB001	--	1.66
RF305	blue	PB001	PB001	--	1.57

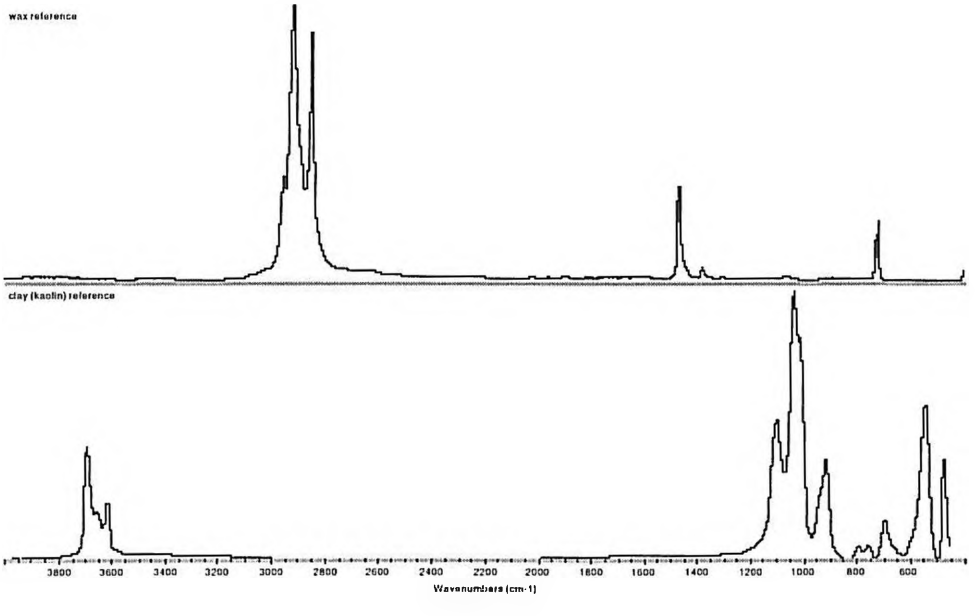
Pencil	Color	IR assignments	UV/VIS assignments	EDS data	TiO2/Si02
RF306	violet	--	PR081/PV001	--	1.89
RF307	blue	PB015	PB015	Cu, Cl	1.10
RF308	violet	PR170	PV003, PR170	Fe	0.86
RF309	violet	PR081, PR170	PR081/PV001	--	0.50
RF310	violet	PR170	PR170	Fe	0.92
RF311	orange	PY001, PO005/16	PY003/PY001	Fe	0.20
RF312	orange	PY001, PR004	--	--	1.18
RF313	blue	PB015	--	--	0.04

OTHER PENCIL COMPONENTS

Analyses to identify organic pigments also revealed the presence of other materials that were beyond the scope of work. This section briefly describes these materials.

Wax and clay

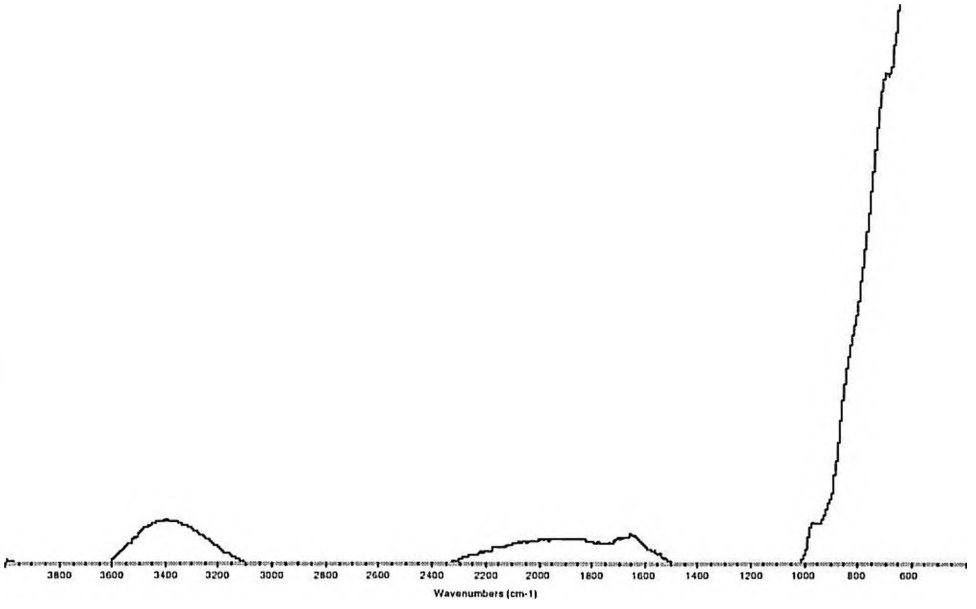
Wax and clay were identified by FTIR analysis as components of each pencil lead. Representative FTIR spectra are shown below: wax (top spectrum) and clay (bottom spectrum). Identification of the specific type of wax and clay were beyond the scope of this project and was not undertaken. Types of clay in the pencil samples differed between manufacturers, but were consistent within each manufacturer group (e.g, Si/Al ratios and the presence or absence of Mg).



Titanium dioxide pigment

Titanium dioxide was suggested by FTIR sample spectra of insoluble fractions– particularly pale tints – as a broad absorption around 600 wavenumbers (see spectrum below). X-ray diffraction analysis would confirm the presence and type (anatase or rutile) of titanium dioxide.

The presence of titanium was confirmed by SEM-EDS analysis of the insoluble sample fractions in the majority of pencils. The relative amount of titanium in each sample is listed in Appendix A-3, as a ratio of the peak area of the major titanium x-ray peak to the major silicon x-ray peak.



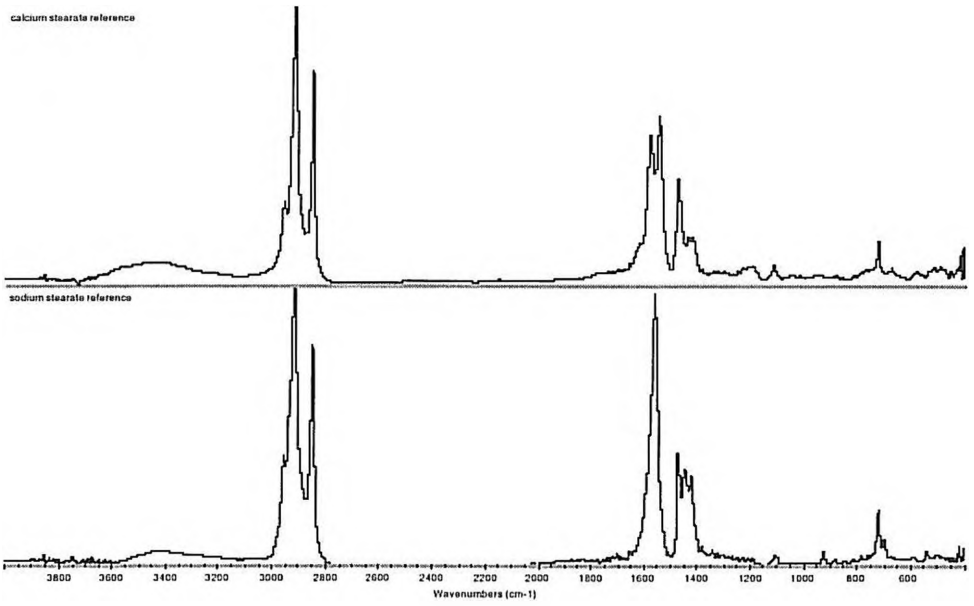
Other inorganic components

FTIR analysis showed the presence of manganese pyrophosphate (PV016) and Prussian blue (PB027). SEM-EDS showed the presence of elements associated with inorganic pigments, including iron (Fe), zinc (Zn), and chromium (Cr).

Stearates

Some samples also contain stearates (salts of stearic acid). Spectral searching gave high probability matches for two stearates – calcium stearate (top) and sodium stearate (bottom) – used individually

or in combination; however, these materials were beyond the project scope, and confirmation of specific stearates (and other fatty acid esters) was not undertaken.



SIGNIFICANT CONCLUSIONS

This program explored the composition of artists' colored pencils, and developed a simple analytical scheme for detection and identification of organic pigments in pencils. The technique involves extraction of pigments in suitable solvents, recrystallization from solution by evaporation, and identification by Fourier transform infrared microspectroscopy (FTIR). The technique was successful in identifying over 466 instances of single and mixed organic pigments in 291 pencils.

FTIR offers significant advantages over analysis of organic pigments by UV/VIS solution spectrophotometry. Foremost is the existence of hundreds of standard reference spectra that are available commercially and through shared spectral libraries within the art conservation science community. These spectral libraries simplify identification of specific pigments; similar libraries of UV/VIS spectra were not located. Second is the rich visual content of infrared spectra– a forest of unambiguous peaks that vary in position and intensity – that directly convey differences in chemical structure. Third is the ability to analyze specific pigments through selective sampling of recrystallized components. Fourth is the comparability of data across solvent fractions, unlike UV/VIS data,

which is solvent dependent. FTIR also is amendable to analysis of samples prepared by sublimation. Sublimation involves heating a sample between a glass microscope slide and cover glass until organic pigments convert directly from the solid state to gaseous state. The sublimate then condenses on the underside of the cooler cover glass, and recrystallizes.

UV/VIS solution spectrophotometry (UV/VIS) was included as a step in the analytical scheme, but, ultimately was not used for primary identification of pigments, being reserved instead for confirmation of identifications made by FTIR. UV/VIS analysis presents certain drawbacks, including incompatibility across solvent fractions, the effect of suspended materials,and the inability to separate individual components for analysis without resorting to many additional extractions.

Additional information about inorganic constituents (e.g., clay and titanium dioxide) and associated ions (e.g., Fe, Cl, Cu, etc.) helped with interpretation of sample spectra and confirmation of specific pigments, and was obtained using scanning electron microscopy with energydispersive spectrometry (SEM-EDS). Iron oxides (browns, yellows, oranges, and reds) were inferred from the presenceof Fe in many samples.

Research limitations

Potential research limitations that could affect the ability to identify all organic pigments in the test pencils were considered at the outset of the project. In practice, the following limitations were encountered.

Extractions for twenty-one pencils gave no colored solution, and FTIR analysis of the remaining insoluble fractions failed to detect organic pigments. The reason(s) for no identification may be the absence of organic pigments, the presence of organic pigments below detection limits or pigments obscured by other pigments or additives, and/or the use of inorganic pigments. Inclusion of sulfuric acid extractions likely would have dissolved remaining organic pigments, but the resulting sample would have been unsuitable for analysis by FTIR. Another factor that may have adversely affected solvent extractions was the inclusion of fatty acid salts, such as calcium and sodium stearates; these and other unidentified emulsifying, or wetting, agents may have affected dissolution of organic pigments, and certainly complicated interpretation of resulting spectra.

While the FTIR reference spectra allowed unambiguous determination of pigments that are orare not present in the samples, the absence of comprehensive FTIR reference spectra for organic pigments prevented identification by FTIR of five pigments that were detected in thirteen pencils. Added to the project scope was additional work to acquire ninety-nine raw organic pigments samples not represented in our libraries, and to create standard reference spectra for these pigments; this work enabled identification of many pigments. Also added to the project scope were upgrades to

high-resolution editions of existing Hummel Polymer, Coatings Technology, and Polymer Additives spectral libraries; these upgrades doubled the resolution of standard reference spectra from 8 cm^{-1} to 4 cm^{-1}, enabling identification of additional pigments.

RECOMMENDATIONS FOR FURTHER WORK

This project

Of course, the principal recommendation for further work is to identify the five (5) detected but as yet unidentified pigments in thirteen (13) pencils, and the colorants used in the twenty-one (21) pencils where no organic pigments were detected. Identification of the detected but unidentified pigments would involve obtaining additional FTIR reference spectra, either from raw pigment samples (or spectra) provided by pigment companies, or other commercial FTIR libraries. Several color pencil manufacturers have expressed interest in providing additional pigments for use as reference standards. Identification of the colorants in the twenty-one pencils would be helped by this work, but probably also would require preparation and analysis of a larger initial sample in order to increase the amount of organic pigments (if present) to the detection limit of FTIR.

Other related work could include determination of various crystalline forms of phthalocyanine, specific salts of Rhodamines and triphenyl methanes, determination of other inoganic pigments and compounds in the pencils, and correlation of data with the results of lightfastness testing.

Recommendations for further work also would include a study of the efficacy of sublimation as a means to isolate individual pigments for FTIR analysis. This work could be started on the raw pigment samples that were collected as part of this project. This work also would be useful in characterizing organic pigments in samples from actual works of art, where sample size often is one or more orders of magnitude less than the 40-50 mg used for this study.

Other projects

Another recommendation of this report is to coordinate this project with efforts currently underway elsewhere to characterize organic pigments using Raman microspectroscopy. Ramanis a technique that is complementary to, but much more costly than, FTIR.

Note: It should be noted that the Principal Investigator is interested, willing, and able to undertake additional work that is deemed useful by the ASTM D01.57 subcommittee.

ACKNOWLEDGEMENTS

The Principal Investigator gratefully acknowledges the assistance of the following people and companies who contributed to the success of this project.

First and special thanks is given to Nicholas Zammuto, Research Assistant, who prepared solvent extractions and collected and analyzed the majority of the vast amount of spectroscopic data contained in this report. Without Nick's professional dedication and diverse capabilities the project would not have attained its present breadth and depth. For this reason, Nick has received – no, earned – the title, Co-Principal Investigator.

The following interns worked diligently to collect data. MK Lalor (SUNY Albany) assisted with initial administrative tasks, prepared each sample for optical microscopy, and collected FTIR for dried solvent extracts. Jessica Turner (Massachusetts College of Liberal Arts) prepared solvent extractions and collected UV/VIS spectra. Catherine Courigneaux (Williams College) examined and collected an image of each pencil sample by optical microscopy.

Thanks to the Chemistry Department at Williams College for use of the Hewlett Packard diodearray spectrophotometer. Nancy Piatczyc and the Bronfman Science Center at Williams College for use of the scanning electron microscope facility.

The following companies provided samples of raw pigments that proved essential to the success of the project: Sun Chemical (Cincinnati, OH 45232), Magruder Color Company (Elizabeth, NJ 07208), and Kremer Pigments, Inc. (New York, NY 10012). Special thanks is given to Dr. George F. Kremer who provided extensive MSDS information on the pigment samples provided by his company. Chris Draves at Nicolet Instrument Corporation (Madison, WI 53711) searched FTIR spectra for the unknown pigments against Nicolet's extensive database of spectral libraries.

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Thanks also are due to Co-Technical Program Managers Joy Turner Luke and Mark Gottsegen for their learned counsel during the preparation and execution of this work, and to Anne McKlindon of ASTM/ISR contracts for administrative assistance throughout the project.

APPENDICES

Appendix A – Tables of Summary Data

1 – FTIR Assignments (by pencil)

2 – UV/VIS Assignments (by pencil)

3 – SEM-EDS data for insoluble fractions (by pencil)

4 – SEM-EDS data for selected samples

Appendix B – FTIR spectra

1 – FTIR sample spectra (by pencil)

2 – FTIR reference spectra (by Color Index name group)

3 – FTIR reference spectra transparencies (by Color Index name group)

Appendix C – UV/VIS spectra

1 – UV/VIS sample spectra (by pencil)

Appendix D – Digital images of pencil leads (written to CD-ROMs, by pencil number)

APPENDIX A- 1: FTIR ASSIGNMENTS

Pencils are listed by their alpha-numeric code number and color in visible light. Pigments observed by FTIR in each of the four fractions from the solvent extraction process, are listed by Color Index Name. The Prefix 'U' indicates an unidentified pigment. The suffix 'T' indicates that the pigment was observed in a trace quantity. The suffixes SMA and PTA on PR081 indicate matches to reference spectra referring to various forms of a molybdenum containing accessory salt.

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction		Insoluble fraction	
LB001	purple	PV001	.	PV001	.	PR048:2	.	.	
LB002	red-purple	PV001	.	PV001	.	PR048:2	.	PR048 T	
LB003	red-purple	PV001	.	PR048:2	.	PR048:2	.	.	
LB004	red	.	.	PV001	.	PR048.4	.	PR048 T	
LB005	orange	PR112	.	.	.	PY013	.	PY013	
LB006	orange	PO013	.	PO013 T	.	PO013	.	PO013	
LB007	orange	PR004	PO013 T	.	.	PO013	.	PO013	
LB008	orange	PR004	.	.	.	.	.	.	
LB009	yellow	PYO13	.	.	.	PY013	.	PY013	
LB010	red	.	.	.	.	PR048:2	.	.	
LB011	red	PO013	.	PR048:4	PR048.2	PR048:2	PR048.4	.	
LB012	red	PO013	.	PR048:4	PR048.2	PR048.4	PR048:2	PO013	
LB013	red	PR112	.	PR112 T	.	PR112	.	PR112	
LB014	red	PY003	.	PR048:4	.	PR048.2	.	PO013	
LB015	pink	.	.	.	.	PR048:2	PO013	.	
LB016	pink	PR081 PTA	PV001	.	.	PR048:2	.	PR048 T	
LB017	purple	PR081 PTA	PV001	PV001	PR081 PTA	PR048:2	.	.	
LB018	red	.	.	.	.	PR048:2	.	PR048.2	
LB019	violet	.	.	.	.	PR048:2	.	PR048.2	
LB020	orange	.	.	PR048:4	.	PR048:2	PY013	PY013	
LB021	violet	PV001	.	.	.	PR048:2	.	.	
LB022	purple	.	.	.	.	.	.	PV023	
LB023	purple	PR081 PTA	.	PV001	.	PR081 PTA	.	.	
LB024	pink	.	.	.	.	PR048:2	.	.	
LB025	pink	.	.	.	.	.	.	.	
LB026	peach	PR112	PY001	.	.	.	.	.	
LB027	purple	PV001	.	PV001	.	PR081 PTA	PV001	PB015	
LB028	red-violet	.	.	.	.	PR048:2	.	.	
LB029	dark blue	.	.	.	.	.	.	PB015	
LB030	light blue	.	.	.	.	.	.	PB015	

Pencil	Color	Chloroform frnction		Methanol fraction		DMP fraction		Insoluble fraction	
LB031	light blue	0	0	PBOOI	0	0	0	0	0
LB032	dark blue	0	0	PBOOt	PB027	PBOOI	PB027	PB001	PB027
LB033	blue	0	0	0	0	0	0	PB015	0
LB034	purple	PVOOI	0	PVOOt	PROB!	PROB!	PVOOt	PB015	0
LB035	blue	PYOOI	0	0	0	0	0	PB015	0
LB036	dark blue	0	0	0	0	PB015	0	PBOIS	0
LB037	dark blue	0	0	0	0	PB015	0	PB015	PV023
LB038	J;,>rCen	PY001	0	0	0	0	0	PB015	0
LB039	light blue	0	0	PBOOI	0	0	0	0	0
LB040	J;,>reen	0	0	0	0	0	0	PG007	0
LB041	blue0green .		0	0	0	PB015	PG007	PB015	PG007
LB042	dark blue	PBOOl	0	PBOOI	PB027	PBOOt	PB027	PB001	PB027
LB043	green0blue	PY003	0	0	0	0	0	PBOIS	0
LB044	yellow	PY013	0	0	0	0	0	0	0
LB045	pink	PYOOl	0	0	0	0	0	0	0
LB046	light purple	0	0	0	0	0	0	0	0
LB047	peach	PRl 12	P0013	0	0	0	0	0	0
LB048	dark orange	P0013	0	0	0	P0013	0	P0013	0
LB049	yellow	PY001	0	PYOOt T	0	PYOOt	0		0
LBOSO	orange	PR112	P0013		0	P0013	0	P0013	0
LBOSI	light orange	P0013	0	PR048:2	0	PR048:2	0	PY013	0
LBOS2	green	PYOOJ	0	0	0		0	PG007	0
LA053	yellow	PY003	0	0	0		0	0	0
LA054	yellow	PYOOI	PY003	0	0	PY003	0	0	0
LA055	yellow	PY074	0	0	0		0	0	0
LA056	yellow	PY013	0	0	0	PY013	0	PY013	0
LA057	orange	PYOOI	0	0	0		0	P0034	0
LA058	blue		0		0	PB015	0	PBOJS	0
LA059	orange	P0013	0	ll 210d	0	U 210d	0	P0013T	0
LA060	orange	P0013	0		0		0	P0013	0
LA061	orange		0	P0034	0	P0034	0	P0034	0
LA062	orange		0		0	0	0	00	0
LA063	red0orange	PR003	0	PR003 T	0	PR003	0	0	0
LA064	light purple	0	0	00	0	0	0	PR122	0
LA065	blue	00	0		0		0	0	0
LA066	reel	PRl 12	0	0	0	PRI12	0	PRI12	0
Lt\067	violet0red	0	0	PV019	0	PV019	0	PV019	0
LA068	pink	PR112	0	0	0	PR170	0	PR170 T	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction		Insoluble fraction	
LA069	red0violet	0	0	0	0	PR122	0	PR122	0
LA070	red	PRl 12	0	0	0	PRl12 T	0	0	0
Lt\071	red	0	0	PV019	0	PR170	PV019	PV019	0
LA072	pink	0	0	PR081 SMA	0	PR081 SMA	0	0	0
LA073	pink	0	0	0	0	0	0	UNIDENTIFIED	0
LA074	pink	PR009	0	0	0	0	0	0	0
LA075	pink	PY003	0	0	0	U 222d	0	0	0
LA076	pink	PY003	0	0	0	0	0	0	0
LA077	red0violet	U 261c	PV001	PVOOl T	0	PR081	0	0	0
LA078	purple	PR081 PTA.		PVOOl	0	PR081	0	0	0
LA079	light violet .		0	0	0	PR081C	PR170	PV016	0
LA080	purple	PV001	0	PVOOl	0	PR081 C	PV001	0	0
LA081	purple	0	0	PV003A	0	PV003A	0	0	0
LA082	light purple	0	0	0	0	0	0	PV023	0
LA083	light purple	0	0	0	0	0	0	PV023	0
LA084	blue	0	0	0	0	0	0	0	0
LA085	purple	0	0	0		PV023	0	PV023	PB015
LA086	blue	PBOOl	0	PBOOl	0	PBOOl	0	0	0
LA087	blue	0	0	0	0	PB015 T	0	PB015	0
LA088	light blue	0	0	0	0	0	0	PB015 T	0
LA089	light blue	0	0	0	0	0	0	0	0
LA090	light blue	0	0	0	0	0	0	–	0
LA091	green0blue .		0	0	0	PB015	0	0	0
LA092	blue	0	0	0	0	PB015	0	PB015	0
LA093	blue	0	0	0	0	0	0	PB015	0
LA094	blue01:,rreen .		0	0	0	PB015	PG007	PB015	PG007
LA095	light blue	0	0	0	0	PB015 T	PG007T	PBOlS T	PG007T
LA096	blue0green	PYOOl	0	0	0	PB015	0	PB015	0
LA097	green	0	0	0	0	PG007	0	PG007	0
LA098	green	PYOOl	0	0	0	PG007	0	PG007	0
LA099	green	PYOOl	PY003	PY003T	0	PY003 T	0	0	0
LA100	yellow	0	0	0	0	PY074	0	0	0
LA101	dark peach	PRl 12	0	0	0	0	0	0	0
LA102	brown	0	0	0	0	PR146	0	0	0
LA103	red0brown.		0	0	0	PR170	0	PR170	0
LA104	violet 0 brown	U 261c	0	0	0	U 261c	0	0	0
RC106	yellow	0	0	0	0	PY083	0	PY083	0
RC107	orange	P0013	0	0	0	P0013	PY013	PY013	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction		Insoluble fraction	
RC108	orange	PR! 12	0	U 210d	0	U 210d	0	0	0
RC109	orange	PY001	PR009	0	0	PY001	U 210d	0	0
RC110	orange	0	0	0	0	U 210d	0	PR168	0
RC111	red	PR004	0	PR004 T	0	PR004	0	0	0
RC112	red	0	0	0	0	PR009	0	0	0
RC113	pink	PR004	0	PR004 T	0	PR004	0	0	0
RC114	pink	0	0	0	0	PR112	0	PR168	0
RC115	red	PR112	0	0	0	PR023	0	PR112	PR023
RC116	violet	0	0	0	0	0	0	PR023	0
RC117	pink	0	0	0	0	0	0	PV019	0
RC118	pink	0	0	0	0	0	0	UNIDENTIFIED	0
RC119	violet	PRl 12	0	PR048:4	0	PR048.4	PR048:2	PV019 T	0
RC120	violet	0	0	PR048:4	0	PR048.4	PR048.2	0	0
RC121	purple	0	0	0	0	PR202	0	PR202	0
RC122	pink	0	0	0	0	PV019	0	PV019	0
RC123	purple	0	0	0	0	0	0	PR202	0
RC124	purple	0	0	0	0	PV019	0	PV019	0
RC125	purple	0	0	0	0	PR122	0	PR122	0
RC126	purple	PVOOl T	0	PV001	0	PR081	PR122	PR122	0
RC127	purple	0	0	0	0	PR122	0	PV023	0
RC128	purple	0	0	0	0	0	0	PV023	PBOIS
RC129	purple	0	0	0	0	PV023 T	0	PV023	0
RC130	blue	0	0	0	0	PV023	PB015 T	PV023	PB015
RC131	blue	0	0	0	0	PB015	0	PB015	0
RC132	blue	0	0	0	0	PB015	0	0	0
RC133	blue	0	0	0	0	PB060	0	PB060	0
RC134	blue	0	0	0	0	PB015	PR202	PB060	0
RC135	blue	0	0	0	0	PB015	0	PB015	0
RC136	blue	0	0	0	0	0	0	PB015 T	PB060
RC137	blue	0	0	0	0	0	0	PB060	0
RC138	blue	PBOOl	0	PB001	0	PB001	0	PG007	0
RC139	blue	0	0	0	0	PB015	PG007	PG007	PB015
RC140	blue	0	0	0	0	PBOlS	0	PBOlS	0
RC141	blue	0	0	0	0	PBOlS	0	PB015	0
RC142	green	0	0	0	0	PB015	PG007	PG007	PBOlS
RC143	blue	0	0	0	0	PBOlS	0	PG007	PB015 T
RC144	1:,rrecn	0	0	0	0	0	0	PG007	0
RC145	!:,'Teen	PYOOl	PY003	0	0	0	0	PG007 T	0
RC146	1:,rrcen	PY003	0	0	0	0	0	0	0
RC147	!:,'TCCn	P0013	PY003	0	0	PY003	0	PB015 T	0
RC148	b'Tecn	P0013	PY003	0	0	PY003	P0013	0	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction		Insoluble fraction	
RC149	yellow	0	0	0	0	U 149d	0	UNIDENTIFIED	
RC150	blue	0	0	0	0	0	0	PB015	0
RC151	pink	0	0	0	0	PR209	0	PR209	0
RC152	red	PR022	0	0	0	PR022	0	PR022	0
RC153	violet	0	0	0	0	PR209	0	PR202	0
RC154	blue	0	0	0	0	PBDIS	0	PBDJS	0
RC155	blue	0	0	0	0	0	0	0	0
RC156	!,'Teen	PY003	0	0	0	PY003	0	PY003 T	0
RC157	peach	0	0	0	0	0	0	0	0
RD158	orange	PR112	PO016	PO016	0	PO016	0	0	0
RD159	orange	PRl12	PO016	PO016	0	PO016	0	PO016	0
RD160	orange	PRl 12	PO016	0	0	0	0	0	0
RDl61	red	PR112	PY001	0	0	0	0	0	0
RD162	red	PR003	0	PR003	0	PR003	0	0	0
RD163	pink	PR! 12	0	PR112	0	PRl12	0	PR112	0
RD164	pink	0	0	0	0	0	0	0	0
RD165	pink	PRl12	PO016	0	0	0	0	–	0
RD166	pink	PRl12	0	0	0	0	0	0	0
RD167	violet	PRl12	0	PR04B:4	0	PR048.4	0	0	0
RD168	violet	PRl12	0	PR048:4	0	PR048.2	0	0	0
RD169	violet	PR048.4	0	PR048:4	0	PR048.4	PR048:2	0	0
RD170	violet	0	0	PR048:4	0	PR048.4	0	0	0
RD171	violet	PRl12	0	0	0	0	0	0	0
RD172	violet	0	0	PR048:4	0	PR048.2	0	0	0
RD173	purple	0	0	PR04S:4	0	PR048.4	PV023	PV023	0
RD174	purple	PV00l	0	PVO0J	PRQS1	PV00I	PROS!	PROS! T	0
RDJ75	purple	0	0	0	0	0	0	PV016	0
RD176	purple	0	0	0	0	0	0	PV016	0
RD177	purple	PV001	0	P\1001/PROBl	PRS7.1	PROB!	PV001	PB015 T	0
RDl78	purple	0	0	U 195m	0	P\1019	PR122	0	0
RD179	purple	0	0	0	0	0	0	PV016	0
RDIB0	purple	0	0	PR057	0	PV003B	0	PB0JS T	0
RDIBI	purple	0	0	0	0	PVD19	0	PV019 T	0
RD182	blue	0	0	0	0	PV019	0	PB015 T	0
RD183	blue	0	0	U 195m	0	PBD15	U 195m	PB0JS	PV023
RD184	blue	0	0	0	0	0	0	PV016	0
RD1S5	blue	0	0	0	0	0	0	0	0
RDIS6	blue	0	0	0	0	0	0	0	0
RD1S7	blue	0	0	0	0	0	0	0	0
RDlSS	blue	0	0	PV003	['B015 T	PV003A	0	PB0JS	0
RDIS9	blue	0	0	0	0	PV019	0	PB015 T	0

Pencil	Color	Chloroform fraction		Methanol fraction		D1\0IF fraction		Insoluble fraction	
RD190	blue	PV0J9T	0	0	0	PB015	PV019	PB015	0
RD191	blue	0	0	0	0	PB015	0	PB015	0
RD192	blue	0	0	0	0	0	0	PB0lS	0
RD193	blue	PB0lS T	0	0	0	0	0	PB015 T	0
RDl94	blue	0	0	PR057	0	PB0IS	PR057	PB015	0
RD195	blue	0	0	U 195m	0	PBOIS	U 195m	PBDIS	0
RDl96	blue	0	0	0	0	0	0	0	0
RD197	blue	0	0	0	0	PB015	0	PB0IS	0
RD198	blue	PB0lS	0	0	0	PB015	0	PB015	0
RD199	blue	0	0	0	0	PB015	PG007	PB0l 5	PG007
RD200	blue	0	0	0	0	PB0IS T		PB015	PG007
RD201	blue	0	0	0	0	0	0	PG007	0
RD202	green	0	0	0	0	PG007	0	PG007	0
RD203	b'Teen	PY00I	0	0	0	0	0	PG007T	0
RD204	orange	0	0	0	0	PO036	0	PO036	0
RD205	red	PRl 12	0	0	0	0	0	0	0
RD206	peach	0	0	0	0	0	0	0	0
RD207	reel	PRl 12	0	0	0	PR112	0	0	0
RD208	violet	0	0	0	0	0	0	PV016	0
RD209	violet	PR! 12	0	0	0	PRl 12	0	0	0
RE210	orange	0	0	0	0	U 210d	0	0	0
RE211	orange	PO013	0	0	0	PO0l3	0	PO013	0
RE212	orange	0	0	PO034	0	PO034	0	PO034	0
RE213	orange	PR004		PR004	0	PR004	0	PR004	0
RE214	red	PR003		PR003	0	PR003	0	PR003	0
RE215	red	PR! 12		PRl12	0	PR112	0	PRl 12	0
RE216	pink	PRl 12			0	PRl70	0	PRl70 T	0
RE217	violct	PR112		PR112T	0	PR112	0	PRl 12	0
RE218	violet	0	0	0	0	PR170	PV019	PV019	0
RE.219	pink	PR081 T	0	PROSl SMA	0	PR081SMP.		PR081T	0
RE.220	**pink**	0	0	0	0	PR209	0	0	0
RE221	pink	PR009	0	0	0	0	0	0	0
RE222	pink	PY003	0	0	0	U 222d	0	0	0
RE223	peach	PY003	0	0	0	0	0	0	0
RE.224	1mrplc	P\1001	0	PV00l	0	P\1001	PR081	0	0
RE.225	purplc	P\!001	0	PV00J	0	PV00J	0	0	0
RE226	purple	0	0	0	0	PRl70	0	PV016	0
RE.227	purple	P\1001	0	PV00l	0	PV00l	P\1003	PV003	0
RE228	purple	0	0	PV003 T	0	PV003A	0	PV003 **T**	0
RE229	purple	0	0	0	0	**PR146**	PV023	PV023	0
RE230	purple	0	0	0	0	0	0	0	0
									0
									0
									0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction		Insoluble fraction	
RE231	purple	0	0	0	0	PV023	0	PV023	0
RE232	blue	PB001 T	0	PB001	0	PB001	0	PB001	0
RE233	blue	PB015 T	0	0	0	PB015	0	PB0lS	0
RE234	blue	0	0	0	0	0	0	UNIDENTIFIED	0
RE235	blue	0	0	0	0	0	0	0	0
RE236	blue	0	0	0	0	PB0lS	0	PB015	0
RE237	blue	0	0	0	0	PB0lS	0	PB015	0
RE238	blue	0	0	0	0	PB015	0	PB015	0
RE239	blue	0	0	0	0	PB015	0	PB015	0
RE240	blue	0	0	0	0	PB015	PG007	PB015	PG007
RE241	blue	0	0	0	0	0	0	0	0
RE242	green	PY001	0	0	0	PB015	0	PB015	0
RE243	green	PY074	0	0	0	PB0lS	PY003	IPB0lS	0
RE244	green	PY001	PY003	0	0	PB015	PY001	PB015	0
RE245	,green	PY001 T	0	0	0	PG007	0	PG007	0
RE246	J,>TCC0	PY003	0	0	0	PG007	0	PG007	0
RE247	!:,>TCCn	PY001	0	0	0	PB0lS	0	PB015	0
RE248	!:,>Teen	PY013	0	0	0	0	0	PY013	0
RE249	rreen	PY074	0	0	0	PY074	0	0	0
RE250	green	PY074	0	0	0	PY074	0	PB015 T	0
RE251	green	PY001	PY003	PY003	0	0	0	PG007T	0
RE252	l,,rreen	PY074	0	0	0	0	0	0	0
RE253	!:,TfCCn	PY074	0	0	0	PY083	0	PY083	0
RE254	green	PY001	0	0	0	PB0lS	0	PB015 T	0
RE255	brown	PO013	PY001	0	0	0	0	0	0
RE256	yellow	PY074	PO013	0	0	0	0	0	0
RE257	red	PR112	0	0	0	0	0	0	0
RE258	red	PR112	0	0	0	0	0	0	0
RE259	violet	PR146 T	0	0	0	PR146	0	0	0
RE260	violet	0	0	PR170	0	PR170	0	PR170	0
RE261	violet	U 261c	0	0	0	U 261C	0	U 261c	0
RF262	blue	PB027	0	0	0	PB027	0	PB027	0
RF263	blue	PB001	0	PB001	0	PB001	0	0	0
RF264	blue	0	0	0	0	PB015	0	PB0lS	0
RF265	blue	0	0	PB001 T	0	0	0	0	0
RF266	blue	PY003	0	0	0	PG007	PB0015	PB0lS	0
RF267	blue	PY003	0	PB001	0	PB0lS	PB001	PB015	0
RF268	green	PY003	0	PB001	0	PY003	0	PB015	0
RF269	orange	0	0	0	0	u PO00S/01(.	0	PO00S/16	0
RF270	blue	0	0	0	0	PB015 T	0	PB0lS	0
									0
									0

0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction		Insoluble fraction	
RF271	orange	PR004	0	PR004	0	PR048.2	0	0	0
RF272	red	PY074	PY00l	0	0	PR048:2	0	PO00S/16	0
RF273	red	PY001	PY003	PY003	0	PY003	0	PR170	0
RF274	red	0	0	0	0	PRl70	0	PR170	PO00S/1(
RF275	pink	PR004	0	PR048.2	0	PR048:2	0	PR048.2	0
RF276	pink	PR004	PV001	PR081 SMA	0	PR048:2	PR081 SMA	0	0
RF277	violet	0	0	PR081	0	PR081	0	PR170	0
RF278	purple	PV0Ol	0	PV001	IP RO Ill	PV00l	0	0	0
RF279	purple	PV001	0	P\1001	IPRO Bl	PV00l	0	PB015	0
RF280	blue	PB0Ol	0	PB0Ol	0	PB00J	0	0	0
RF281	pink	0	0	0	0	0	0	0	0
RF282	1,rray	0	0	0	0	0	0	PB027	0
RF283	brown	PY00I	PR170	0	0	PR170	0	PR170	0
RF284	peach	PR004	0	PR004	0	0	0	0	0
RF285	purple	0	0	0	0	0	0	0	0
RF286	1,rreen	PY00I	PR004	PY001 T	0	PY001	PB027	PB027	0
RF287	blue	0	0	0	0	0	0	0	0
RF288	pink	0	0	PROS! SMA	0	PR0lll Sl'vrA	0	0	0
RF289	pink	0	0	PR0BI SMA	0	PR081 SMA	0	0	0
RF290	violet	0	0	PR081 SMA	0	PR081 SMA	0	0	0
Rr0291	purple	0	0	0	0	PR170	0	PB015 T	PR170
Rr0292	orange	PY00l	PR004	PY00l T	0	PY00l	0	0	0
RF293	green	PY0OI	PY003	PY003	0	PY003	0	0	0
Rr0294	green	PY001	PY003	PY003 T	0	PY003	0	0	0
RF295	purple	0	0	PB00l T	0	PV003B	0	0	0
RF296	purple	PV00l BASE	0	P\1001	PR081 SMA	PV00l	0	0	0
RF297	violet	PV00I CYCLIZED ESTER	0	PV00I	PR081SMJ\	0 PR0BISMJ.	0	0	0
RF298	blue	0	0	0	0	0	0	0	0
RF299	violet	0	0	0	0	PR048:2	0	0	0
RF300	pink	0	0	0	0	0	0	0	0
RF301	violet	0	0	0	0	PR048.2	0	0	0
RF302	blue	0	0	0	0	0	0	0	0
RF303	blue	0	0	0	0	PB027	0	PB027	0
RF304	blue	0	0	PB00J T	0	0	0	0	0
RF305	blue	0	0	PB00I T	0	0	0	0	0

RF306	violet	0	0	0	0	0	0	0	0
RF307	blue	PB0lS	0	0	0	PB0JS T	0	PB0IS	0
RF308	violet	0	0	0	0	PR170	0	PR170	0
RF309	violet	0	0	PR081 SMA	0	PR081 SMA	0	PR170	0
RF310	violet	0	0	0	0	PR170	0	PR170T	0
RF311	or:ingc	PY001	0	PY00J	0	PY00l	PO005/1(	PO00S/16	0
RP312	orange	PY00l	PR004	0	0	PYO0I	0	0	0
RP313	blue	0	0	0	0	0	0	PB015 T	0

APPENDIX A0 2: UV/VIS ASSIGNMENTS

Pencils are listed by their alpha0numeric code and color in visible light Pigments observed by UV-VIS solution spectrophotometry in each of the three liquid fractions from the extraction process are listed by their Color Index name. The suffix 'T' indicates that the pigment was observed in a trace quantity. The suffn;:es 'u','<', and 'cl' following PB015 indicate slight shifts in the position of the peaks in the UV/VIS spectrum, which may give information on the shade of the phthalocyanine used (red shade or green shade, PB15:1, :2, :3, :4). Further analysis would be required in order to distinguish these forms of PB015 with confidence.

Pencil	Color	Chloroform Fraction		Methanol Fraction		DMF Fraction	
LB00l	purple	PR081 /PV001	0	PV001	0	PR048	PR081
LB002	red0purple	PR081 /PV001	0	PV001	0	PR048	PR081
LB003	red0purple	PR081 /PV001	0	PR048	0	PR048	PR081
LB004	red	0	0	P\!001	0	PR048	0
LB00S	orange	PR112	PY003/PY001	0	0	0	0
LB006	orange	PO013	0	0	0	0	0
LB007	orange	PR.004	0	0	0	0	0
LB008	orange	0	0	0	0	PR004	0
LB009	}'cllow	0	0	PR003T	PR048	0	0
LB0l0	reel	0	0	PR048	0	PR048	0
LBOl 1	red	PO013	0	PR048	0	PR048	0
LB012	reel	PO013	0	PR048	0	PR048	0
LB013	red	PR112	0	0	0	PRl 12	0
LB014	red	PY003/PY001	0	PR048	0	PR048	0
LB015	pink	PO013	0	PR048	0	PR048	0
LB016	pink	PR081/PV001	0	*P\!001*	PR081	PR048	0
LB017	purple	PR081 /PV001	0	PV00l	0	PR048	PR081
LB018	red	0	0	0	0	0	0
LB019	violet	0	0	PR048	0	PR048	0
LB020	orange	0	0	PR048	0	PR048	PY013
LB021	violet	0	0	PR048	0	PR048	0
LB022	purple	0	0	0	0	PR081 /PV001	0
LB023	purple	0	0	P\!001	0	PR081	0
LB024	pink	0	0	0	0	0	0
LB025	pink	0	0	PR081	0	PR081	0
LB026	peach	PRl 12	0	0	0	0	0
LB027	purple	PR081 /PV001	0	P\!001	0	PR081	PR081
LB028	red0violet	0	0	PR048	0	PR048	0
LB029	dark blue	0	0	0	0	0	0
LB030	light blue	0	0	0	0	0	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
LB031	light blue	0	0	PB00I	0	0	0
LB032	dark blue	0	0	PB00l	0	PB001	0
LB033	blue	0	0	0	0	0	0
LB034	purple	PROSI/PV00l	0	PV00J	0	PR081	0
LB035	blue	PY003/PY001	0	0	0	0	0
LB036	dark blue	0	0	0	00	0	0
LB037	dark blue	0	0	0	0	PB015	0
LB038	1,rrccn	PY003/PY001	0	0	0	0	0
LB039	light blue	0	0	0	0	0	0
LB040	green	0	0	0	0	0	0
LB041	bluc01„rrccn	0	0	0	0	PB015	0
LB042	dark blue	0	0	PB00J	0	PB00l	0
LB043	green0blue	PYD03/PY0D1	0	0	0	PB015<	0
LB044	yellow	0	0	0	0	0	0
LB045	pink	PY003/PY001	0	0	0	0	0
LB046	light purple	0	0	0	0	0	0
LBD47	peach	0	0	0	0	0	0
LB048	dark orange	POD13	0	0	0	PO013	0
LB049	yellow	PYD03/PY001	0	0	0	PY003/PY001	0
LB0S0	orange	PO013	0	0	0	PO013	0
LB051	light orange	PO013	0	PR04B	0	PR048	0
LB052	bttcen	0	0	0	0	0	0
LA053	yellow	PY003/PY001	0	PY003/PYDD1	0	PY003/PY001	0
LA054	yellow	PY003/PY0D1	0	PY003/PY001	0	PY003	0
LAOSS	yellow	PYD74	0	0	0	PY074	0
LAD56	yellow	0	0	0	0	PY013	0
LA057	orange	ri'Y003/PY001	0	0	0	0	0
LA0SB	blue	0	0	0	0	PB0lSU	0
LA059	orange	PO013	0	U 210d	0	U 210d	0
LA060	orange	PO013	0	0	0	0	0
LA061	orange	0	0	PO034	0	PO034	0
LA062	orange	0	0	0	0	0	0
LA063	red0orange	PR003	0	PR003	0	0	0
LA064	light purple	0	0	0	0	0	0
LA065	blue	0	0	0	0	0	0
LA066	red	PR112	0	0	0	0	0
LA067	violet0red	0	0	0	0	PV019	0
LAD68	[Jink	PR112	0	0	0	PR170	0
LA069	red0violet	0	0	0	0	PR122	0
LA070	red	PRl 12	0	0	0	0	0
LAD71	red	PRl 12	0	0	0	PV019	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
LA072	pink	0	0	PR081	0	PR081	0
LA073	pink	0	0	0	0	PR209	0
LA074	pink	PR009	0	0	0	0	0
LA075	pink	PY003/PY001	0	0	0	U 222d	0
LA076	pink	PY003/PY001	0	0	0	0	0
LA077	red0violet	U 261c	PR081 /PV001	PV001	0	PR081	0
LA078	purple	PR081 /PV001	0	P\!001	0	PR081	0
LA079	light violet	PR112 (trace)	0	0	0	PR170	0
LA080	purple	PR0B1 /PV0O1	0	PVO0l	0	PR081	0
LA081	purple	0	0	PV003	0	PV003	0
LA082	light purple	0	0	0	0	0	0
LA083	light purple	0	0	0	0	0	0
LA084	blue	0	0	0	0	0	0
LA0BS	purple	0	0	0	0	PV023	0
LA086	blue	0	0	PB001	0	PB00l	0
LA087	blue	0	0	0	0	PB015<	0
LA088	light blue	0	0	0	0	PB015u	0
LA089	light blue	0	0	0	0	0	0
LA090	light blue	0	0	0	0	0	0
LA091	brreen0blue	0	0	0	0	PB015	0
LA092	blue	0	0	0	0	PB015U	0
LA093	blue	0	0	0	0	PB015U	0
LA094	blue0green	0	0	0	0	PB015	PG007
LA095	light blue	0	0	0	0	PB015	0
LA096	blue0brrccn	PY003/PY001	0	0	0	PB015U	0
LA097	green	0	0	0	0	PG007	0
LA098	brrecn	PY003/PY001	0	0	0	PG007	0
LA099	brrcen	PY003/PY001	0	PY003/PY001	0	PY003/PY001	0
LA100	yellow	0	0	0	0	PY074	0
LA101	dark peach	0	0	0	0	0	0
LA102	brown	0	0	0	0	PR146	0
LA103	**red0brown**	PR112	0	0	0	PR170	0
LA104	violct0browr	U 261c	0	0	0	PR170	0
RC106	yellow	0	0	0	0	0	0
RC107	orange	PO013	0	0	0	PY013	PO013
RC108	orange	PRl 12	0	U 210d	0	U 210d	0
RC109	orange	PY003/PY001	0	PY001A	0	PY003/PY001	0
RC110	orange	0	0	0	0	U 210d	0
RC111	red	PR004	0	PR004	0	PR004	0
RC112	**red**	0	0	0	0	0	0
RCl 13	pink	PR004	0	PR004	0	PR004	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
RC114	pink	0	0	0	0	PR022	0
RC115	red	PRl 12	0	0	0	PRl 12	0
RC116	violet	PR112	0	0	0	U 260d	0
RC117	pink	0	0	PR048	0	PV019	0
RC118	pink	0	0	0	0	0	0
RCl 19	violet	PRl 12	0	PR048	0	PR048	0
RC120	violet	0	0	PR048	0	PR048	0
RC121	purple	0	0	0	0	PR202	0
RC122	pink	0	0	0	0	PV019	0
RC123	purple	0	0	0	0	0	0
RC124	purple	0	0	0	0	0	0
RC125	purple	0	0	0	0	PR122	0
RC126	purple	PROB1 /PV001	0	PV001	0	PR122	PR081
RC127	purple	0	0	PV003T	0	PR122	PV023
RC128	purple	0	0	0	0	0	0
RC129	purple	0	0	0	0	0	0
RC130	blue	0	0	0	0	PV023	0
RC131	blue	0	0	0	0	PB015	0
RC132	blue	0	0	0	0	0	0
RC133	blue	0	0	0	0	0	0
RC134	blue	0	0	0	0	PB015	PR202
RC135	blue	0	0	0	0	PB015	0
RC136	blue	0	0	0	0	0	0
RC137	blue	0	0	0	0	PB015d	0
RC138	blue	0	0	0	0	PB001	0
RC139	blue	0	0	0	0	PB015	0
RC140	blue	0	0	0	0	PB015	0
RC141	blue	0	0	0	0	PB015	0
RC142	green	0	0	0	0	PG007	PB015
RC143	blue	0	0	0	0	PB015	0
RC144	green	0	0	0	0	0	0
RC145	green	PY003/PY001	0	0	0	0	0
RC146	green	PY003/PY001	0	0	0	0	0
RC147	green	PY003/PY001	0	0	0	PY003	0
RC148	f:,l"een	PY003/PY001	0	0	0	PY003	0
RC149	}"ellow	0	0	0	0	U 149d	0
RC150	blue	0	0	0	0	0	0
RC151	pink	0	0	0	0	PR209	0
RC152	red	PR009	0	0	0	PR022	0
RC153	violet	0	0	0	0	PV209	0
RC154	blue	0	0	0	0	PB015	0

Pencil	Color	Chloroform fraction		I\0fethanol fraction		DMr fraction	
RC155	blue	0	0	0	0	0	0
RC156	!:,l"feen	PY003/PY001	0	0	0	PY003	0
RC157	peach	0	0	0	0	0	0
RD158	orange	PO016	0	PO016	0	PO016	0
RD159	orange	PO016	0	PO016	0	PO016	0
RD160	orange	PO016	0	0	0	0	0
RD161	red	PRl 12	PY003/PY001	0	0	0	0
RD162	red	PR003	0	PR003	0	PR003	0
RD163	pink	PRl 12	0	PR112	0	PR112	0
RD164	pink	0	0	0	0	0	0
RD165	pink	PO016	PR112	0	0	0	0
RD166	pink	PRl 12	0	0	0	0	0
RD167	violet	PRl 12	0	PR048	0	0	0
RD168	violet	PRl 12	0	PR048	0	0	0
RD169	violet	0	0	PR048	0	PR048	0
RD170	violet	0	0	PR048	0	0	0
RD171	violet	PR112	0	PVO0l	0	PV00l	0
RD172	violet	0	0	PR048	0	PR048	0
RD173	purple	0	0	PR048	0	PV023	0
RD174	purple	PR0S1 /PV001	0	PV00l	PR081	PR081	0
RD175	purple	0	0	0	0	0	0
RD176	purple	0	0	0	0	0	0
RD177	purple	PR0S1/PV001	0	PR081	PV001/PR081.	PR081	0
RD178	purple	0	0	U 195m	0	PV019	0
RD179	purple	0	0	0	0	0	0
RD180	purple	0	0	PV00l /PR081	0	PV003	0
RD181	purple	0	0	0	0	PV019	0
RD182	blue	0	0	0	0	PV019	0
RD183	blue	0	0	U 195m	0	PB015	0
RD184	blue	0	0	0	0	0	0
RD185	blue	0	0	0	0	0	0
RD186	blue	0	0	0	0	0	0
RD187	blue	0	0	0	0	0	0
RD188	blue	0	0	PV003T	0	PV003	0
RD189	blue	0	0	0	0	PV019	0
RD190	blue	0	0	0	0	PV019	0
RD191	blue	0	0	0	0	PB015	0
RD192	blue	0	0	0	0	PB0l Sd	0
RD193	blue	0	0	0	0	0	0
RD194	blue	0	0	PR048	0	PB015	0
RD195	blue	0	0	U 195m	0	PB015	PR170T

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
RD196	blue	0	0	0	0	0	0
RD197	blue	0	0	0	0	PB015	0
RD198	blue	0	0	0	0	PB015	0
RD199	blue	0	0	0	0	PB015	0
RD200	blue	0	0	0	0	PB015	0
RD201	blue	0	0	0	0	0	0
RD202	green	0	0	0	0	PG007	0
RD203	green	PY003/PY001	0	0	0	PY003/PY001	0
RD204	orange	0	0	0	0	PO036	0
RD205	red	PR112	0	0	0	0	0
RD206	peach	0	0	0	0	0	0
RD207	red	PR112	0	0	0	PRl 12	0
RD208	violet	0	0	0	0	0	0
RD209	violet	PRl 12	0	0	0	0	0
RE210	orange	0	0	0	0	U 210d	0
RE211	orange	PO013	0	0	0	PO013	0
RE212	orange	PO013	0	PO034	0	0	0
RE213	orange	PR004	0	PR004	0	PR004	0
RE214	reel	PR003	0	PR003	0	PR003	0
RE215	red	PRl 12	0	PRl 12	0	PR112	0
RE216	pink	PRl 12	0	0	0	PR170	0
RE217	violet	PR112	0	PR112	0	PR112	0
RE218	violet	0	0	0	0	PV019	0
RE219	pink	0	0	PR081	0	PR081	0
RE220	pink	0	0	0	0	PR209	0
RE221	pink	PR009	0	0	0	0	0
RE222	pink	PY003/PY001	0	0	0	U 222d	0
RE223	peach	PY003/PY001	0	0	0	0	0
RE224	purple	0	0	PV001	0	PR081	PRl 12
RE225	purple	PR081 /PV001	0	PV00t	0	PR081	0
RE226	purple	0	0	0	0	PR170	0
RE227	purple	PR081 /PV001	0	PV001	0	PR081	0
RE.228	purple	0	0	0	0	PV003	0
RE229	purple	0	0	0	0	PR146	0
RE230	purple	0	0	0	0	0	0
RE231	purple	0	0	0	0	PV023	0
RE232	blue	0	0	PB001	0	PB001	0
RE233	blue	0	0	0	0	PB015<	0
RE234	blue	0	0	0	0	0	0
RE235	blue	0	0	0	0	0	0
RE236	blue	0	0	0	0	PB015	0

Pencil	Color	Chloroform fraction		Methanol fraction		DlVIF fraction	
RE237	blue	0	0	0	0	PB015	0
RE238	blue	0	0	0	0	PB015<	0
RE239	blue	0	0	0	0	PB015U	0
RE240	blue	0	0	0	0	PG007	PB015
RE241	blue	0	0	0	0	0	0
RE242	1&rreen	PY003/PY001	0	0	0	PB0lSU	0
RE243	een	PY003/PY001	0	0	0	PB0lS	0
RE244	green	PY003/PY001	0	0	0	PY003/PY001	PB0lS
RE245	i,rreen	PY003/PY001	0	0	0	PG007	0
RE246	1:,rrcen	PY003/PY00 I	0	0	0	PG007	0
RE247	1,rreen	PY003/PY001	0	0	0	PB0IS	0
RE248	1,rrecn	0	0	0	0	0	0
RE249	1:,rrecn	PY074	0	0	0	PY074	0
RE250	green	PY074	0	0	0	PY074	0
RE251	ween	PY003/PY001	0	0	0	0	0
RE252	U,rreen	PY074	0	0	0	0	0
RE253	i,rrecn	0	0	0	0	0	0
RE254	green	PY003/PY001	0	0	0	PB015	0
RE255	brown	PY003/PY001	0	0	0	0	0
RE256	yellow	PY074	0	0	0	0	0
RE257	red	PRl 12	PY003/PY0011	0	0	0	0
RE258	red	PR112	0	0	0	0	0
RE259	violet	0	0	0	0	PR146	PR004
RE260	violet	PRl 12	0	0	0	0	0
RE261	violet	U 261c	0	0	0	PB00l	0
RF262	blue	0	0	PB027	0	PB027	0
RF263	blue	0	0	0	0	PB00l	0
RF264	blue	PB0l5 suspcnsior	0	0	0	PB015	0
RF265	blue	0	0	PBO0l	0	0	0
RF266	blue	PB0l5 suspensior	0	0	0	0	0
RF267	blue	PB0l5 suspcnsior	0	PB00l	0	PB015	0
RF268	1,rrcen	PY003/PY001	0	PB001	0	PY003	0
RF269	orange	0	0	0	0	PO016	0
RF270	blue	0	0	0	0	0	0
RF271	orange	PR004	0	PR004	0	PR004	0
RF272	red	PY074	PY003/PY001	PY00lA	0	PR048	0
RF273	red	PY003/PY001	0	0	0	PY003	0
RF274	red	PO0l3	0	0	0	PR170	0
Rf275	pink	PR004	0	PR004	0	PR048	0
RF276	pink	PR004	0	PR081	0	PR081	0
Rf277	violet	Sllspens1on	0	PROS!	0	PR081	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
Rr278	purple	PV001	0	PVO0I	PR081	PV001	0
Rr279	purple	PR08t /PV001	0	PV001	PR0BI	PVO0I	0
RF280	blue	suspension	0	PB0OI	0	PB001	0
RF2BI	pink	suspension	0	PVO0t	0	0	0
RF2S2	:i,tt:ay	suspension	0	PB00t	0	0	0
RF2S3	brown	PY003/PY001	suspension	PV003T	0	PR170	0
Rr284	peach	PR004	0	0	0	0	0
RF2SS	purple	PR0B1 /PV00 I	0	0	0	0	0
RF2B6	b,recn	PY003/PY001	0	0	0	PY003/PY001	0
Rr287	blue	0	0	0	0	0	0
RF2B8	pink	suspens10n	0	PROS1	0	PR081	0
RF2B9	pink	suspens10n	0	PROBI	0	PR081	0
RF290	violet	suspension	0	PROBI	0	PR081	0
RF291	purple	0	0	0	0	PR170	0
RF292	orange	PY003/PY001	0	0	0	PY003/PY001	0
Rr293	bTfeen	PY003/PYOOI	0	0	0	PY003/PY001	0
Rr294	ll:,TfCCn	PY003/PY001	0	0	0	PY003/PY001	0
RF295	purple	suspension	0	PB001	0	PV003	0
Rr296	purple	PROB1 /PV001	0	PV001	PROS!	PV001	0
RF297	violet	PV001	0	PVO0I	PROBI	PROBI	0
RF298	blue	0	0	0	0	0	0
RF299	violet	0	0	0	0	PR048	0
Rr:300	pink	0	0	0	0	0	0
RF301	viukt	0	0	0	0	PR04B	0
RF302	blue	0	0	0	0	PVOl9	0
Rr303	blue	0	0	0	0	PB027	0
RF304	blue	suspension	0	PB00I	0	0	0
RF305	blue	suspension	0	PB00I	0	0	0
RF306	violet	PROS I /PV001	0	PV00I	0	0	0
Rr307	blue	suspension	0	0	0	PB015	0
RF308	violet	suspension	0	PV003T	0	PRl70	0
RF309	violet	PROS I /PV001	0	PROB!	0	PR081	0
RF310	violet	0	0	0	0	PR170	0
RF311	orange	PY003/PY001	0	0	0	PO036T	0
R[0312	orange	0	0	0	0		0
Rr0313	blue	0	0	0	0		0
		0	0	0	0		0

APPENDIX A 0 3: SEM0EDS data for insoluble fractions (by pencil)

The following table lists the elements detected in the insoluble fraction cf each sample. The values listed were determined by calculating the ratio of the peak area for each element to the peak area for silicon (Si); thus, Si shows a n01malized value of 1.00. The elements listed are sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (CD, potassium (K), calcium (Ca), titanium (Ti), manganese (Mn), copper (Cu), and zinc (Zn).

Pencil	Na	Mir	Al	Si	p	S	a	K	C01	Ti	Fe	Mn	Cu	Zn
LBOOl	0	0	0.71	1.00		0	0	0.08	0	0.1	0.02	0	0	0
LB002	0	0	0.74	1.0	0	0.0	00.01	0.06	00.0	0.4	0.01	0	0	0
LB003	0	0	0.77	1.0	0	0	0	0.1	0	0.11	0.01	0	0	0
LB004	0	0	0.7:	1.0	0	0.0	0	0.09	0.02	0.03	0.02	0	0	0
LB005	0	0	0.71	1.0	0	0	0	0.08	0	0.5(	0.02	0	0	0
LB006	0	0	0.71	1.0	0	0	00.0	0.1C	0	0.01	0.01	0	0	0
LB007	0	0	0.73	1.0	0	0	0.0	0.0	0	0.0(	0.0	0	0	0
LBOOS	0	0	0.73	1.0	0	0	0	O.H	0	0.02	0.0	0	0	0
LB009	0	0	0.78	1.0	0	0	0	0.0	0	0.01	0.0	0	0	0
LB010	0	0	0.73	1.0	0	0	0	0.1	0.0	0.1	0.0	0	0	0
LBOl 1	0	0	0.73	1.0	0	0	0	0.1	0	0.03	0.0	0	0	0
LB012	0	0	0.75	1.0	0	0	00.0	0.0	0	O.lS	0.0	0	0	0
LB013	0	0	0.7,	1.0	0	0	0.03	O. H	0	0.01	0.0	0	0	0
LB014	0	0	0.63	1.0	0	0	0	0.1	0	0.0(	0.0	0	0	0
LB015	0	0	0.7(	1.0	0	0	0	0.1	0	0.61	0.02	0	0	0
LB016	0	0	0.70	1.0	0	0	0	o.m	0	0.38	0.0	0	0	0
LB017	0	0	0.6,	1.0	0	0	0	O.Oi	0.03	0.14	0.01	0	0	0
LB018	0	0	0.6f	1.0	0	0.01	0	0.11	0.0	0.02	0.0	0	0	0
LB019	0	0	0.7:	1.0	0	0	0	0.0	0.01	0.12	0.01	0	0	0
LB020	0	0	0.7'	1.0	0	0	0.0	o.m	0	0.3(	0.02	0	0	0
LB02I	0	0	0.67	1.0	0	0	0	0.08	0.04		0.43	0	0	0
LB022	0	0	0.7□	1.0	0	0	0	0.09	0	0.37	0.02	0	0	0
LB023	0	0	0.71	1.0C	0	0	0	0.1	0	0.12	0.02	0	0	0
LB024	0	0	0.76	1.0C	0	0	0	0.09	0.04	0.63	0.02	0	0	0
LB025	0	0	0.71	1.0	0	0	0	0.1	0	0.2:	0.02	0	0	0
LB026	0	0	0.72	1.0C	0	0	0	0.09	0	o.sc	0.0	0	0	0
LB027	0	0	0.74	1.0C	0	0	0	0.08	0	0.21	0.03	0	0	0
LB028	0	0	0.70	1.0C	0	0	0	0.09	0		0.3(	0	0	0
LB029	0	0	0.74	1.0	0	0	0	0.0C	0	0.45	0.03	0	0	0
LB030	0	0	0.73	1.0	0	0	0	0.08	0	1.3i	0.03	0	0	0
LB031	0	0	0.72	1.0C	0	0	0	0.09	0	0.8(	0.02	0	0	0
LB032	0	0	0.72	1.0	0	0	0	0.07	0	0.12	0.05	0	fl.OS	0
LB033	0	0	0.72	1.0C	0	0	0	0.09	0	0.2	0.02	0	0	0
LB034	0	0	0.75	1.0C	0	0	0	0.09	0	0.2(	0.02	0	0	0
LB035	0	0	0.70	1.0	0	0	0	0.1C	0	0.8(	0.02	0	0	0
LB036	0	0	0.74	1.0	0	0	0	0.1C	0	0.13	0.02	0	0.()2	0
		0												

Pencil	Na	Mg	Al	Si	p	S	a	K	Ca	Ti	Pe	Mn	Cu	Zn
LB037	0	0	0.7(	1.00	0	Zn		0.0	0	0.1	0.02	0	0.0	0
LB038	0	0	0.7(	1.00	0	0		0.0	0	0.33	0.02	0	0	0
LB039	0	0	0.74	1.00	0	0		0.0	0	0.45	0.02	0	0	0
LB040	00	0	0.73	1.00	0	0	0.05	0.0	0	0.55	0.03	0	0	0
LB041	0	0	0.71	1.00	0	0	0.06	0.0	0	0.4(	0.03	0	0	0
LB042	0	0	0.73	1.00	0	0		0.0	0	0.03	0.05	0	0.0	0
LB043	0	0	0.71	1.00	0	0		0.1	0	0.35	0.D	0	trace	0
LB044	0	0	0.70	1.00	0	0		0.1	0	0.61	0.0	0	0	0
LB045	0	0	0.67	1.00	0	0		0.10	0.05	0.39	0.02	0	0	0
LB046	0	0	0.71	1.0C	0	0		0.0	0.05	0.38	0.02	0	0	0
LB047	0	0	0.76	1.0C	0	0		0.1,	0	0.53	0.03	0	0	0
LB048	0	0	0.73	1.0C	0	0	0.0:	0.1	0	0.02	0.03	0	0	0
LB049	0	0	0.76	1.0C	0	0		0.1	0	0.08		0	0	0
LB050	0	0	0.67	1.00	0	0	0.02	0.1	0	0.05	0.02	0	0	0
LB051	0	0	0.72	1.00	0	0		0.0	0	0.63	0.02	0	0	0
LB052	0	0	0.71	1.00	0	0	0.lC	0.1	0	0.47	0.03	0	0	0
LA053	0	0	0.76	1.00	0	0		0.07	0		0.01	0	0	0
LA054	0	0	0.73	1.00	0	0		*0.08*	0		0.01	0	0	0
LA055	0	0	0.73	1.00	0	0		O.Q7	0	0.68	0.06	0	0	0
LA056	0	0	0.77	1.00	0	0	0.03	0.06	0		0.01	0	0	0
LA057	0	0	0.76	1.00	0	0		0.08	0		0.01	0	0	0
LA058	0	0	0.78	1.0(	0	0		0.06	0	0.06	0.01	0	0	0
LA059	0	0	0.7(	1.0(	0	0		0.07	0	0.3(	0.01	0	0	0
LA060	0	0	0.76	1.0(	0	0	0.02	0.05	0	0.34	0.02	0	0	0
LA061	0	0	0.76	1.0C	0	0	0.04	0.06	0		0.02	0	0	0
LA062	0	0	0.76	1.0C	0	0		0.07	0			0	0	0
LA063	0	0	0.77	1.0C	0	0		0.07	0		0.02	0	0	0
LA064	0	0	0.77	1.0C	0	0		0.06	0.03	0.25	0.01	0	0	0
LA065	00.03	0	0.69	1.0C	0	0		0.06	0.02			0	0	0
LA066	0	0	0.77	1.00	0	0	0.0°	0.07	0		0.01	0	0	0
LA067	0	0	0.67	1.00	0	0		0.08	0.06	0.24	0.01	0	0	0
LA068	0	0	0.73	1.00	0	0		0.06	0	0.74	O.O:	0	0	0
LA069	0	0	0.75	1.00	0	0		0.07	0	0.18	0.02	0	0	0
LA070	0	0	0.75	1.00	0	0		0.07	0.02			0	0	0
LA071	0	0	0.75	1.00	0	0		O.OE	0	0.25		0	0	0
LA072	0	0	0.73	1.00	0	0		0.0(	0	0.33		0	0	0
LA073	0.02	0	0.70	1.00	0	0		O.O	0.03	0.73		0	0	0
LA074	0	0	0.75	1.00	0	0		0.04	0.02	1.24	0.07	0	0	0
LA075	0	0	0.72	1.00	0	0		0.07	0	0.65	0.0(	0	0	0
LA076	0	0	0.73	1.00	0	0		0.07	0	0.66	0.04	0	0	0
LA077	0	0	0.77	I.OD	0	0		0.0	0		0.01	0	0	0
LA078	0	0	0.75	1.00	0	0		0.07	0	0.17		0	0	0
LA079	0	0	0.69	1.0(	0.29	0.02		0.09	0.03	0.06		0.21	0	0
LA080	0	0	0.74	1.00	0	0		0.07	0	0.15	0.01	0	0	0
LA081	0	0	0.79	1.00	0	0		0.07	0	0.14	0.02	0	0	0

Pencil	Na	Mg	Al	Si	p	S	a	K	C1	1i	Fe	Mn	Cu	Zn
LA082	0	0	0.7(	1.00	0	0	0	0.06	0	0.58	0	0	0	0
LA083	0	0	0.73	1.00	0	O.G2	0	0.07	0	0.23	0	0	0	0
LA084	0.01	0	0.72	1.00	0	0.08	0	0.06	0	0.12	0.01	0	0	0
LAOBS	0	0	0.73	1.00	0	0	0.02	0.08	0	0.24	0	0	0	0
LA086	0	0	0.76	1.00	0	0	0	0.07	0	0.19	0	0	0	0
LA087	0	0	0.71	l.OC	0	0	0	0.07	0	0.83	0	0	0.02	0
LA088	0	0	0.78	l.OC	0	0	0	0.06	0	0.37	0	0	trace	0
LA089	0	0	0.66	1.00	0	0.32	0	O.o7	0	0.7.3	0	0	0	0.07
LA090	0	0	0.75	1.00	0	0	0	0.06	0	0.25	0	0	0	0
LA091	0	0	0.73	1.00	0	0	0.0i	0.08	0	0.13	0.02	0	0.0,	0
LA092	0	0	0.76	1.00	0	0	0.02	0.08	0	0	0	0	0.02	0
LA093	0	0	0.76	1.00	0	0	0	0.07	0	0.22	0	0	0	0
LA094	0	0	0.73	1.00	0	0	0.14	0.07	0	0	0	0	,trace	0
LA095	0	0	0.75	1.00	0	0	0	0.06	0	0.23	0	0	0	0
LAO%	0	0	0.7(	1.00	0	0	0.03	0.07	0	0	0.02	0	O.Q2	0
LA097	0	0	0.7(	1.00	0	0.03	0.12	0.07	0	0.59	0.01	0	0	0
LA098	0	0	0.6	1.00	0	0	0.23	0.0(	0	0.21	0	0	0	0
LA099	0	0	0.77	1.00	0	0	0	0.07	0	0	0.01	0	0	0
LAlOO	0	0	0.76	1.00	0	0	0	0.07	0	0.48	0.06	0	0	0
LA!Ol	0	0	0.74	1.00	0	0	0	0.0l	0	0	0.12	0	0	0
LA102	0	0	0.64	1.00	0	0	0	0.07	0	0	0.86	0	0	0
LAI03	0	0	0.1,1	1.00	0	0	0	0.09	0	0	0.06	0	0	0
LA104	0	0	0.07	1.00	0	0	0	0.06	0	0	0.05	0	0	0
RC106	0	0.20	0.28	1.00	0	0	0	0	0	1.27	0.02	0	0	0
RC107	0	0.24	0.23	l.OC	0	0	0.04	0.03	0.01	0.20	0.02	0	0	0
RC108	0	0.18	0.31	1.00	0	0	0	0.02	0	0.22	0.02	0	0	0
RCI09	0	0.23	0.26	1.00	0	0	0	0.03	0	0.27	0.02	0	0	0
RC110	0	0.22	0.26	1.00	0	0	0		0	0.22	0.02	0	0	0
RC111	0	0.23	0.23	1.00	0	0	0	0.02	0	0.23	0.02	0	0	0
RC112	0	0.17	0.25	1.00	0	0	0.07		0	0,07	0.80	0	0	0
RC! 13	0	0.20	0.31	1.00	0	0	0	0.02	0	0.16	0.02	0	0	0
RCl 14	0	0.18	0.27	1.00	0	0	0		0.02	1.1,1	O.Q2	0	0	0
RCllS	0	0.21	0.26	1.0C	0	0	0.07		0	0.61	0.02	0	0	0
RCl 16	0	0.16	0.34	t.OC	0	0	0	0,03	0	0.3C	0.02	0	0	0
RC117	0	0.20	0.26	1.00	0	0	0	0	0	0.92	0.02	0	0	0
RC!18	0	0.22	0.20	l.OC	0	0	0	0	0	0.97	0.02	0	0	0
RCl 19	0	0.21	0.19	1.00	0	0.02	0.02	0	0.02	0.51	0.02	0	0	0
RC120	0	U.22	0.22	1.00	0	0.02	0.02	0	O.D3	0.37	0.02	0	0	0
RC121	0	0.17	0.29	1.00	0	0	0.05	0.02	0	0.39	0.02	0	0	0
RC122	0	0.18	0.30	1.00	0	0	0.06	0.02	0.01	0.41	0.02	0	0	0
RC123	0	0.24	0.2C	1.00	0	0	0	0	0	0.81	0.02	0	0	0
RC124	0	0.20	0.25	1.00	0	0.09	0.18	0.02	0	0.53	0.02	0	0	0
RC125	0	0.20	0.26	1.00	0	0	0	0.02	0	0.55	0.03	0	0	0
RC126	0	0.24	0.23	1.00	0	0	0	0.04	0	0.72	0.02	0	0	0
RCl27	0	0.18	0.26	1.00	0	0	0.0.3	0		0.47	0.02	0	0	0
													0	0

Pencil	Na	l'vlg	Al	Si	p	S	a	K	C01	Ti	Fe	Mn	Cu	Zn
RC128	0	0.18	0.2	1.00	0	0	0.G3	0.01	0	0.33	O.O	0	0	0
RC129	0	0.23	0.21	1.00	0	0	0	0.03	0.01	a.is	0.02	0	0	0
RC130	0	0.17	O.2	l.OC	0	0	0.02	0.03	0.02	0.24	0.02	0	0	0
RC131	0	0.17	0.33	I.DC	0	0	0.02	0.03	0.02	0.2E	0.02	0	0.0.	0
RC132	0	0.17	0.29	I.DC	0	0	0	0.01	0	0.92	0.02	0	0	0
RC133	0	0.18	0.28	1.00	0	0	0	0.02	0	0.32	0,0.	0	0	0
RCl34	0	0.20	0.2.3	1.00	0	0	0.06	0.02	0.02	0.43	0.0.	0	0	0
RC135	0	0.18	0.28	1.0(	0	0	0	0,0.	0.0'	0.22	0.o::	0	00	0
RC136	0	0.17	0.33	J.OC	0	0	0	0.0:	0	0.92	0.02	0	0	0
RC137	0	0.23	0.21	1.0C	0	0	0		0	0.72	0.02	0	0	0
RC138	0	0.17	0.34	I.0C	0	0	0.11	0.02	0.01	0.13	0,02	0	0	0
RC139	0	0.2(	0.27	1.00	0	0	0.09	0.03	0.02	0.42	0.02	0	0.01	0
RC140	0	0.24	0.19	1.00	0	0	0	0.02	0	0.63	0.02	0	0	0
RC141	0	0.17	0.29	1.00	0	0	0	0.02	0	0.20	0.02	0	0.02	0
RC142	0	0.17	0.31	1.00	0	0	0.2C		0	0.48	0.02	0	0.01	0
RC143	0	0.20	0.21	1.00	0	0	0.02	0.02	0	0.61	0.02	0	0	0
RC144	0	0.1cJ	0.3(	l.0C	0	0	0.06	0.G3	0	1.18	0.03	0	0	0
RC145	0	0.19	0.3(	1.0(	0	0	0.01	0.G3	0	0.36	0.02	0	0	0
RC146	0	0.13	O.3	1.0(	0	0	0	0.02	0.02	2.14	0.02	0	0	0
RC147	0	0.21	0.23	1.0(	0	0	0	0.02	0	0.63	0.02	0	0	0
RC148	0	0.22	0.24	1.0(	0	0	0	0.03	0	0.43	0.02	0	0	0
RC149	0	0.17	0.33	1.0(	0	0	0	0.02	0.01	0.31	0.02	0	0	0
RC150	0	0.20	0.32	1.0(	0	0	0	0.G3	0	0.28	0.02	0	0.02	0
RC151	0	0.19	0.27	1.0(	0	0	0.08	0.02	0.01	0.2::	0.02	0	0	0
RC152	0	0.20	0.28	1.0C	0	0	0.01	0.03	0	0.16	0.02	0	0	0
RC153	0	0.16	0.29	1.0C	0	0	0.0f	0.03	0.02	0.23	0.02	0	0	0
RC154	0	0.1(	0.33	l.OC	0	0	0	0.02	0.01	0.22	0.02	0	0.01	0
RC155	0	0.1S	0.25	I.DC	0	0	0	0.02	0.02	1.30	0.02	0	0	0
RC156	0	0.21	0.26	1.00	0	0	0	0.02	0	0.21	0.02	0	0	0
RC157	0	O.1	0.32	1.00	0	0	0	0.02	0	0.73	0.03	0	0	0
RD158	0	0.01	0.60	1.00	0	0	0	0.0i	0	0.22	0.02	0	0	0
RD159	0	0.01	0.66	1.00	0	0	0	0.07	0	0.20	0.02	0	0	0
RD160	0	0	0.75	1.00	0	0	0	0.0(	0	0.38	0.01	0	0	0
RD161	0	0.02	0.61	1.00	0	0	0	0.0	0	0.43	0.02	0	0	0
RD162	0	0.0E	0.53	1.00	0	0	0	0.12	0		0.03	0	0	0
RD163	0	0.04	0.55	1.00	0	0	0.03	0.0:	0	0.35	0.02	0	0	0
RD164	0	0	0.77	1.00	0.02	0	0	0.0i	0	0.41	0.03	0.02	0	0
RD165	0	0	0.71	1.00	0	0	0	0.08	0	1.09	0.02	0	0	0
RD166	0	0	0.73	1.00	0	0	0	0.07	0	0.34	0.01	0	0	0
RD167	0	0.0.5	0.49	1.00	0	O.0E	0	0.04	0	0.02	0.23	0	0	0
RD168	0	0	0.74	1.00	0	0	0.01	0.07	0	0.31		0	0	0
RD169	0	0.04	0.55	1.00	0	0.03	0	0.05	0.02		0.01	0	0	0
RDl70	0	0	0.67	1.00	0	0	0	0.07	0	0.42	0.1(	0	0	0
RD171	0	0	0.75	1.00	0	0	0	0.07	0	0.30	0.01	0	0	0
RD172	0.02	0	0.70	1.00	0	0.1	0	0.07	0	1.02	0.01	0	0	0

Pencil	Na	Mg	Al	Si	p	S	Cl	K	Ca	Tl	Fe	Mn	Cu	Zn
RD173	0	0	0.80	1.00	0	0	0.01	0.03	0	0.40	0.01	0	0	0
RD174	0	0	0.74	1.00	0	0	0	0.07	0	0.27	0.01	0	0	0
RD175	0	0	0.70	1.00	0.58	0	0	0.33	0	0.47	0	0.38	0	0
RD176	0	0	0.74	1.00	0.06	0	0	0.12	0	0.37	0	0.06	0	0
RD177	0	0	0.71	1.00	0	0	0	0.06	0	0.15	0.02	0	0	0
RD178	0	0	0.76	1.00	0	0	0	0.05	0	0.10	0.01	0	0	0
RD179	0	0	0.74	1.00	0.03	0	0	0.10	0	0.28	0.02	0.05	0	0
RD180	0	0	0.75	1.00	0	0	0	0.08	0.02	0.24	0.01	0	0	0
RD181	0	0	0.71	1.00	0	0	0	0.08	0	0.84	0.01	0	0	0
RD182	0	0	0.74	1.00	0	0	0	0.08	0	0.43	0.01	0	0	0
RD183	0	0	0.73	1.00	0	0	0.02	0.06	0	0.23	0.01	0	0	0
RD184	0.03	0	0.67	1.00	0.11	0.17	0	0.15	0	0	0	0.10	0	0
RD185	0.02	0	0.67	1.00	0	0.14	0	0.09	0	0.23	0.02	0	0	0
RD186	0	0	0.72	1.00	0.01	(J.04	0	0.06	0	0.86	0.01	0.02	0	0
RD187	0	0	0.77	1.00	0	0.02	0	0.06	0	0.47	0.01	0	0	0
RD188	0	0	0.76	1.00	0	0	0	0.07	0	0.25	0.01	0	0	0
RD189	0	0	0.74	1.00	0	0	0	0.08	0	0.40	0.02	0	0	0
RD190	0	0	0.74	1.00	0	0	0	0.07	0	0.52	0.01	0	0	0
RD191	0	0	0.70	1.00	0	0	0	0.09	0	0.28	0.02	0	0	0
RD192	0	0	0.72	1.00	0	0	0	0.05	0	0.19	0	0	0	0
RD193	0	0	0.72	1.00	0	0	0	0.07	0	0.67	0.01	0	0	0
RD194	0	0	0.75	1.00	0	0	0	0.06	0	0.32	0.02	0	0	0
RD195	0	0	0.79	1.00	0	0	0	0.06	0.01	0.07	0.01	0	0.01	0
RD196	0	0	0.73	1.00	0	0.04	0	0.07	0	0.35	0.03	0	0	0
RD197	0	0	0.70	1.00	0	0	0	0.08	0	0.19	0.02	0	0.02	0
RD198	0	0	0.74	1.00	0	0	0	0.05	0	0.74	0.02	0	0	0
RD199	0	0	0.70	1.00	0	0	0.11	0.13	0.02	0.38	0.03	0	0.02	0
RD200	0	0	0.71	1.00	0	0	0.04	0.09	0	0.24	0.01	0	0	0
RD201	0	0	0.75	1.00	0	0	0	0.05	0.01	0.76	0.01	0	0	0
RD202	0.03	0	0.65	1.00	0	0.19	0.15	0.08	0	0.23	0.01	0	0	0
RD203	0	0.05	0.54	1.00	0	0	0.02	0.06	0	0.25	0.01	0	0	0
RD204	0	0	0.70	1.00	0	0	0.05	0.07	0	0.41	0.03	0	0	0
RD205	0	0	0.67	1.00	0	0.02	0	0.07	0	0.36	0.54	0	0	0
RD206	0	0	0.76	1.00	0	0	0	0.07	0	0.38	0.06	0	0	0
RD207	0	0	0.66	1.00	0	0.01	0.09		0	0.33	0.44	0	0	0
RD208	0	0	0.72	1.00	0.06	0.06	0	0.09	0	0.45	0.13	0.06	0	0
RD209	0	0	0.78	1.00	0	0	0	0.06	0	0.38	0.05	0	0	0
RE210	0	0	0.75	1.00	0	0	0	0.07	0	0.29	0.01	0	0	0
RE211	0	0	0.76	1.00	0	0	0.04	0.06	0	0.28	0.01	0	0	0
RE212	0	0	0.77	1.00	0	0	0.05	0.05	0	0.26	0.01	0	0	0
RE213	0	0	0.77	1.00	0	0	0.09	0.06	0	0	0.01	0	0	0
RE214	0	0	0.77	1.00	0	0	0	0.07	0	0	0.01	0	0	0
RE215	0	0	0.77	1.00	0	0	0	0.06	0	0	0.01	0	0	0
RE216	0	0	0.75	1.00	0	0	0	0.07	0.03	0.60	0.04	0	0	0
RE217	0	0	0.79	1.00	0	0	0.02	0.05	0	0	0.02	0	0	0

Pencil	Na	Mg	Al	Si	p	S	Cl	K	C'l	Tl	Fe	Mn	Cu	Zn
RE218	0	0	0.73	1.00	0	0	0	0.08	0.02	0.30	0.01	0	0	0
RE219	0	0	0.76	1.00	0	0	0	0.05	0	0.22	0.01	0	0	0
RE220	0.02	0	0.68	1.00	0	0.16	0,01	0.07	0.02	0.65	0.01	0	0	0
RE221	0	0	0.74	1.00	0	0	0	0.05	0.02	0.67	0.04	0	0	0
RE222	0	0	0.74	1.00	0	0	0	0.07	0	0.55	0.04	0	0	0
RE223	0	0	0.77	1.00	0	0	0	0.05	0	0.65	0.04	0	0	0
RE224	0	0	0.80	1.00	0	0	0	0.05	0	0	0.01	0	0	0
RE225	0	0	0.78	1.00	0	0	0	0.06	0	0.20	0.01	0	0	0
RE226	0	0	0.72	1.00	0.28	0.02	0	0.06	0.01	0.08	0	0.29	0	0
RE227	0	0	0.78	1.00	0	0	0	0.05	0	0.19	0.01	0	0	0
RE228	0	0	0.78	1.00	0	0.01	0	0.06	0.02	0.13	0.01	0	0	0
RE229	0	0	0.73	1.00	0	0	0	0.05	0	0.50	0.D1	0	0	0
RE230	0.02	0	0.71	1.00	0	0.13	0	0.07	0.02	0.10	0.01	0	0	0
RE231	0	0	0.76	1.00	0	0	0.03	0.07	0.01	0.26	0.02	0	0	0
RE232	0	0	0.75	1.00	0	0	0	0.06	0	0.14	0.01	0	0	0
RE233	0	0	0.74	1.0C	0	0	0	0.06	0	0.73	0.01	0	0.02	0
RE234	0	0	0.69	1.00	0	0.36	0	0.05	0.02	0.76	0	0	0	0.11
RE235	0	0	0.74	1.00	0	0	0	0.06	0	0.62	0	0	0	0
RE236	0.02	0	0.68	1.00	0	0.17	0	0.06	0.03	0.68	0.01	0	0	0
RE237	0	0	0.76	1.00	0	0	0.05	0.05	0	0	0.01	0	0.03	0
RE238	0.02	0	0.69	1.00	0	0.12	0	0.05	0.02	0.37	0.01	0	trace	0
RE239	0	0	0.78	1.00	0	0	0.02	0.06	0	0	0.01	0	0.02	0
RE240	0	0	0.79	1.00	0	0	0.14	0.05	0	0.14	0.01	0	**trace**	0
RE241	0	0	0.76	1.00	0	0	0	0.05	0	0.22	O.G1	0	0	0
RE242	0	0	0.77	1.00	0	0	0.02	0.05	0	0	0.D1	0	0.02	0
RE243	0	0	0.74	1.00	0	0	0	0.05	0	0	0.01	0	0.02	0
RE244	0	0	0.78	1.00	0	0	0	0.07	0	0	0.01	0	0.01	0
RE245	0	0	0.73	1.00	0	0	0.23	0.05	0	0.16	0.01	0	0.01	0
RE246	0	0	0.77	1.00	0	0	0.16	0.05	0.01	0.13	0.D1	0	**trace**	0
RE247	0	0	0.78	1.00	0	0	0	0.06	0	0	0.01	0	0.01	0
RE248	0	0	0.74	1.00	0	0	0.07	0.07	0	0.21	O.D1	0	0	0
RE249	0.02	0	0.75	1.00	0	0.09	0	0.05	0.01	0	0.01	0	0	0
RE250	0.01	0	0.77	1.00	0	0.05	0	0.06	0.02	0	0.01	0	0	0
RE251	0	0	0.80	1.00	0	0	0.01	0.05	0	0	0	0	0	0
RE252	0.01	0	0.74	1.00	0	0.08	0	0.06	0	0.29	0.03	0	0	0
RE253	0	0	0.77	1.00	0	0	0.04	0.07	0	0.31	0.01	0	0	0
RE254	0.01	0	0.50	1.00	0	0	0	0.04	0.04	0.26	0	0	0	0
RE255	0	0	0.76	1.00	0	0	0	0.06	0.02	0	0.07	0	0	0
RE256	0	0	0.78	1.00	0	0	0	0.06	0.03	0	0.03	0	0	0
RE257	0	0	0.72	1.00	0	0	0	0.06	0	0	0.23	0	0	0
RE258	0	0	0.77	1.00	0	0	0	0.06	0	0	0.11	0	0	0
RE259	0	0	0.65	1.00	0	0	0	0.06	0	0	1.04	0	0	0
RE260	0	0	0.78	1.00	0	0	0	0.06	0.03	0	0.05	0	0	0
RE261	0	0	0.79	1.00	0	0	0	0.05	0	0	0.05	0	0	0
RF262	0.05	0	0.77	1.00	0	0.02	0	0	0.18	0.03	0.29	0	0	0

Pencil	Na	Mg	Al	Si	p	S	Cl	K	C'l	1i	Fe	Mn	Cu	Zn
RF263	0.01	0	0.73	1.00	0	0	0	0	0.16	1.64	0.02	0	0	0
RF264	0.02	0	0.73	1.00	0	0	0	0	0.19	1.85	0	0	0.02	0
RF265	0.01	0	0.72	1.00	0	0	0	0	0.20	2.11	0.02	0	0	0
RF266	0	0	0.73	1.00	0	0	0.37	0	0.14	1.88	0	0	0.03	0
RF267	0.02	0	0.71	1.00	0	0	0	0	0.22	1.13	0	0	0.06	0
RF268	0.02	0	0.74	1.00	0	0	0.15	0	0.18	0.24	0	0	0.03	0
RF269	0.01	0	0.73	1.00	0	0	0	0	0.19	1.52	0.02	0	0	0
RF270	0	0	0.73	1.00	0	0	0	0	0.18	2.12	0	0	0	0
RF271	0.03	0	0.75	1.00	0	0	0	0	0.18	1.81	0	0	0	0
RF272	0.01	0	0.74	1.00	0	0.06	0.06	0.01	0.33	0.76	0.02	0	0	0
RF273	0.01	0	0.71	1.00	0	0.03	0.05	0	0.20	0.24	0	0	0	0
RF274	0.01	0	0.67	1.00	0	0	0	0	0.15	0.05	0.01	0	0	0
RF275	0.02	0	0.75	1.00	0	0.04	0.03	0	0.26	1.59	0.02	0	0	0
RF276	0.02	0	0.75	1.00	0	0	0	0	0.33	2.86	0	0	0	0
RF277	0.02	0	0.69	1.00	0	0.03	0	0	0.20	1.48	0	0	0	0
RF278	0.01	0	0.81	1.00	0	0.03	0	0.01	0.11	0.04	0.01	0	0	0
RF279	0	0	0.75	1.00	0	0	0	0	0.23	2.34	0	0	0	0
RF280	0.03	0	0.80	1.00	0	0.03	0	0.02	0.11	0.53	0.01	0	0	0
RF281	0.02	0	0.76	1.00	0	0	0	0	0.17	2.33	0	0	0	0
RF282	0	0	0.69	1.00	0	0	0	0	0.26	3.19	0.09	0	0	0
RF283	0.01	0	0.67	1.00	0	0	0	0	0.16	0.05	0.73	0	0	0
RF284	0.02	0	0.77	1.00	0	0	0	0	0.27	2.96	0.29	0	0	0
RF285	0.02	0	0.74	1.00	0	0	0	0	0.17	2.05	0.01	0	0	0
RF286	0.02	0	0.74	1.00	0	0	0.11	0	0.16	2.21	0	0	0	0
RF287	0	0	0.80	1.00	0	0	0	0	0.14	1.39	0	0	0	0
RF288	0.01	0	0.77	1.00	0	0	0	0.02	0.17	1.60	0	0	0	0
RF289	0	0	0.86	1.00	0	0	0	0	0.32	3.80	0	0	0	0
RF290	0.02	0	0.73	1.00	0	0.02	0	0	0.18	1.90	0.02	0	0	0
RF291	0	0	0.72	1.00	0	0	0	0	0.24	2.16	0.02	0	0	0
RF292	0.02	0	0.75	1.00	0	0	0	0	0.23	1.95	0	0	0	0
RF293	0.01	0	0.75	1.0C	0	0	0	0	0.24	0.91	0.02	0	0	0
RF294	0,01	0	0.78	1.00	0	0.03	0	0	0.13	0.37	0.01	0	0	0
RF295	0	0	0.71	1.00	0	0.03	0	0	0.20	1.69	0	0	0	0
RF296	0.01	0	0.76	1.00	0	0	0	0	0.30	2.99	0.02	0	0	0
RF297	0	0	0.77	1.00	0	0.04	0	0	0.20	0.29	0.01	0	0	0
RF298	0	0	0.74	1.00	0	0	0	0	0.34	1.92	0	0	0	0
RF299	0	0	0.72	1.00	0	0	0	0	0.48	2.68	0.14	0	0	0
RF300	0.02	0	0.74	1.00	0	0	0	0	0.33	2.69	0.03	0	0	0
RF301	0	0	0.68	1.00	0	0	0	0	0.48	4.13	0.12	0	0	0
RF302	0.02	0	0.73	1.00	0	0	0	0	0.19	1.63	0	0	0	0
RF303	0	0	0.74	1.00	0	0	0	0	0.11	2.58	0.15	0	0	0
RF304	0	0	0.72	1.00	0	0	0	0	0.30	1.66	0	0	0	0
RF305	0.01	0	0.73	1.00	0	0	0	0	0.27	1.57	0.02	0	0	0
RF306	0	0	0.73	1.00	0	0	0	0	0,30	1.89	0	0	0	0
RF307	0	0	0.75	1.00	0	0	0.34	0	0.21	1.10	0.02	0	0.06	0

Pencil	Na	Mg	Al	Si	p	S	0	K	C.0i	TI	Fe	Mn	Cu	Zn
RF308	0.01	0	0.72	1.00	0	0	0	0	0.21	0.86	0.26	0	0	0
RF309	0.02	0	0.74	1.00	0	0	0	0	0.22	0.50	0.01	0	0	0
RF310	0	0	0.69	1.00	0	0	0	0	0.26	0.92	0.83	0	0	0
RF311	0.01	0	0.74	1.00	0	0.02	0	0	0.24	0.20	0.40	0	0	0
RF312	0.01	0	0.73	1.00	0	0.02	0	0	0.23	1.18	0.28	0	0	0
RF313	0.01	0	0.80	1.00	0	0	0	0	0.25	0.04	0.02	0	0	0

APPENDIX A0 4: SEM0EDS data for selected samples

The absence or presence of certain elements, such as chlorine, was determined for representative recrystallized samples using SEM0EDS. SEM0EDS also was used to identify cations associated with salts of organic pigments such as PR048 and Rhodamires Y and B. The symbol '0' indicates that no elements having an atomic number greater than 10 were observed in any significant quantity. Elements in parentheses were observed in minor or trace quantities.

Pencil	Color	Chloroform Fraction		Methanol Fraction		DMP fraction	
LB001	purple::	PVOOI	\XI	0	0	PR048:2	Ca, \XI (Na)
LB002	red0purple	0	0	0	0	PR048:2	Ca, Na, \Y,/
LB003	reel0purple	0	0	PR048:2	Ca, Na	PR048:2	Ca, Na, \Y./
LB004	red	0	0	0	0	PR048.4	Mn,Ca,Na
LB008	orange	PR004	a	0	0	0	0
LB010	red	0	0	0	0	PR048:2	Ca (Na)
LB011	red	0	0	PR048:4/:2	Mn,Ca	PR048:2/:4	Mn (Ca)
LB012	red	0	0	PR048:4/2	Mn, Ca, (Na)	0	0
LB014	reel	0	0	PR048:4	Mn,Ca	PR048.2	Ca (J\lln)
LB015	pink	0	0	0	0	PR048:2	Ca (Na)
LB016	pink	0	0	0	0	PR048:2	Ca (Na, \X1)
LB017	purple	0	0	0	0	PR048:2	Ca (\X1)
LBOIS	red	0	0	0	0	PR048:2	C:1
LB019	violet	0	0	0	0	PR048:2	C'l
LB020	orange	0	0	PR048:4	i\fo, (Ca, Na)	PR048:2	Mn, Ca (Na)
LB021	violet	0	0	0	0	PR048:2	Ca (Na)
LB028	red0violet	0	0	0	0	PR048:2	Ca,Na
LB048	dark orange	P0013	a	0	0	P0013	Cl
LB049	yellow	0	0	0	0	PY001	o (Cl, S, Na)
LB051	light orange	0	0	PR048:2	Ca (Na)	PR048:2	Ca, Na (J\lln)
LA067	violet0red	0	0	0	0	PV019	(Cl, S, Na)
LA069	red0violet	0	0	0	0	PRI22	S (Cl, Fe, Na)
LA071	reel	0	0	PV019	(S, Na)	0	0
LA074	pink	0	0	0	0	0	0
LA078	purple	PRDBl PTA	W(CI)	0	0	0	0
LADBl	purple	0	0	0	0	PVDOJA	\XI, S, (Cl, Na
LA086	blue	PB001	o (Cl, Na)	0	0	0	0
LJ\096	blue0brrccn	0	0	0	0	PB015	Cl,Cu
LAlOO	rellow	0	0	0	0	PY074	o (S)
RC106	i•ellow	0	0	0	0	PY083	Cl, (Na)
RCI 10	orange	0	0	0	0	U 210d	Cl, Br
RCt 12	reel	0	0	0	0	PR009	Fc,CI
		0	0	0			

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
RClIS	eccl	0	0	0	0	PR023	Cl
RC119	violet	0	0	PR048:4	Mn (Ca, Na)	PR048.4	Mn (Ca)
RC120	violet	0	0	PR048:4	Mn (Ca)	PR048.4	Mn (Ca)
RC121	pueplc	0	0	0	0	PR202	Cl, (S)
RCl33	blue	0	0	0	0	PB060	Na
RCl49	yellow	0	0	0	0	U 149d	Cl, (Na, S)
RC151	pink	0	0	0	0	PR209	Cl, (S)
RC152	eccl	PR022	Cl (PR009)	0	0	PR022	Cl (PR009)
RC156	gccen	0	0	0	0	PY003	a
RD!SB	orange	0	0	0	0	PO016	o
RD159	ornngc	0	0	0	0	PO016	o
RD162	red	PR003	o (Cl)	PR003	o (Cl, S, Na)	0	0
RD167	violet	0	0	PR048:4	Mn (Ca)	PR048.4	Mn
RD168	violet	0	0	PR048:4	Mn (Ca)	PR048.2	(Mn, Ca, Na)
RD169	violet	0	0	PR048:4	Mn (Ca)	PR048.4	Ca, Mn (Na)
RD170	violet	0	0	PR048:4	Mn (Na)	PR048.4	Na,Ca,Mn
RD172	violet	0	0	PR048:4	Mn (Ca)	PR048.2	Mn,Ca,Na
RD173	purple	0	0	PR048:4	Mn (Ca)	PR048.4	Na,Mn,Ca
RDJBO	purple	0	0	0	0	PV003B	Mo, (S)
RD183	blue	0	0	U 195m	S, Cl,Na	0	0
RDJSB	blue	0	0	PV003	(S, Cl, Cu, Fe, Na;	0	0
RD194	blue	0	0	PR057	S, Na, (Cl)	0	0
RD197	blue	0	0	0	0	PBOIS	Cu ,S,CI
RD198	blue	PB0IS	Cl,Cu	0	0	0	0
RD202	green	0	0	0	0	PG007	Cl,Cu
RE210	mange	0	0	0	0	U 210d	o
RE212	orange	0	0	PO034	f0c, Cr, Ni, Cl	0	0
RE213	orange	0	0	PR004	Cl,S	PR004	Cl
RE214	red	0	0	0	0	PR003	o
RE215	red	0	0	PR112	Cl, (S, Na)	0	0
RE222	pink	0	0	0	0	U 222d	Cl
REZZS	purple	0	0	PV0OI	W(Na)	PV00t	\VI, (S, Cl, Na
RE231	1rnrple	0	0	0	0	PV023	Cl (S)
RE232	blue	0	0	PB00JB	0,'i/, Na)	PB00t	WI, S (Cl)
RE237	blue	0	0	0	0	PB0IS	CI,S,Cu
RE259	violet	0	0	0	0	PR146	Cl, (S, Na)
RE261	violet	U 261c	o (Cl)	0	0	U 261C	Cl, S (Na)
RF262	blue	PB027	Fe	0	0	PB027	Fe
RF263	blue	0	0	PB001	S 0,V/, Na)	PBOOI	\VI, S, (Cl)
RF272	red	0	0	0	0	PR048:2	Ca
RF274	red	0	0	0	0	PR170	0

Pencil	Color	Chloroform fraction		Methanol fraction		DMF fraction	
RF275	pink	0	0	PR048.2	Na	PR048:2	Ca (Na)
RF276	pink	0	0	0	0	PR048:2	Ca (Na)
RF277	violet	0	0	0	0	PR081	Mo, (S)
RF278	purple	0	0	0	0	PVOOl	Mo, (S)
RF283	brown	0	0	0	0	PR170	(S)
RF289	pink	0	0	PROB! SMA	Cl,S,Na	PROS! SMA	Mo, (S)
RF292	oran!,te	0	0	0	0	PYOOl	0
RF296	purple	0	0	0	0	PVOOI	Mo, (S)
RF299	violet	0	0	0	0	PR048:2	Ca,Na