The coupling of reflectance and XRF spectroscopies in the shade determinations of the carmine Admiral issue of Canada (Scott 106)

Richard Judge

Second International Symposium on Analytical Methods in Philately
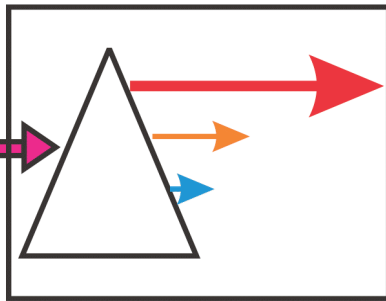
Chicago, IL

Nov 20-22, 2015
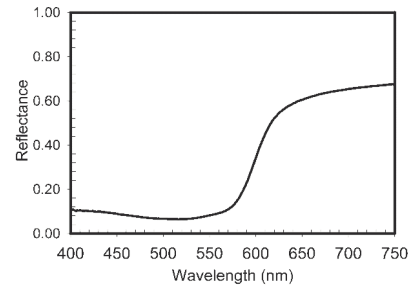
White Light Source

Sample

Spectrometer

Computer Processing

Reflectance Spectrum

Mathematical Processing

5.10 Value

$+-/*\Sigma$ 5.57 R-BG

-0.51 Y-PB

(a)   (b)   (c)   (d)   (e)   (f)   (g)

Reflectance

1.00
0.80
0.60
0.40
0.20
0.00
400 450 500 550 600 650 700 750
Wavelength (nm)
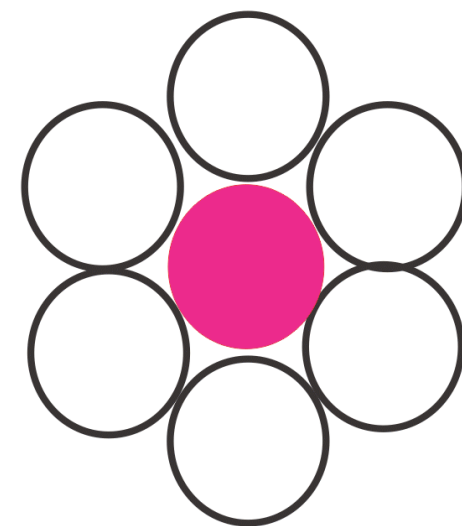
Steps used to determine the CIE and Romney parameters

Range: 200 to 1100 nm
Resolution: ~0.1nm FWMN
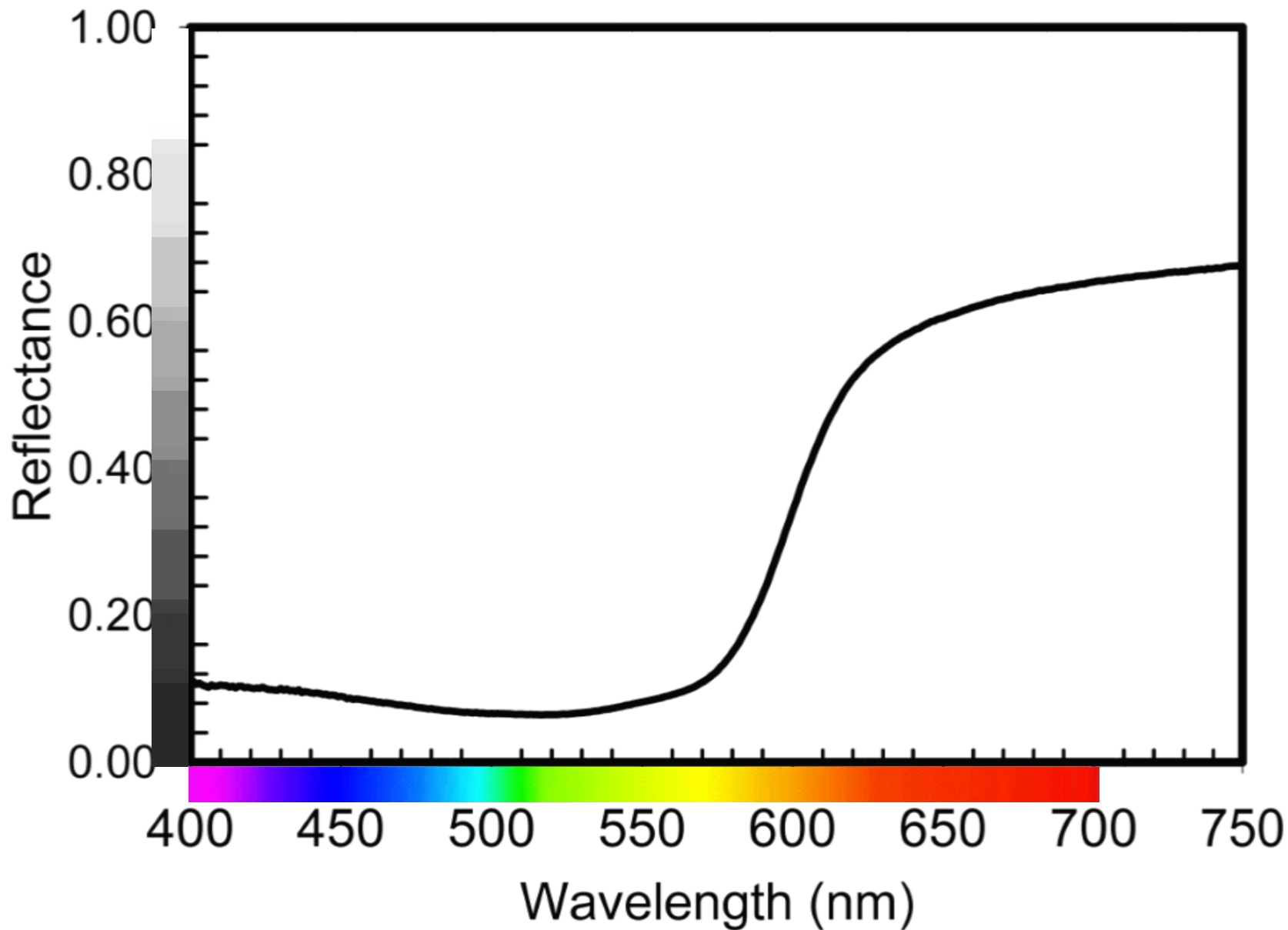
Approximate
Illumination Spot
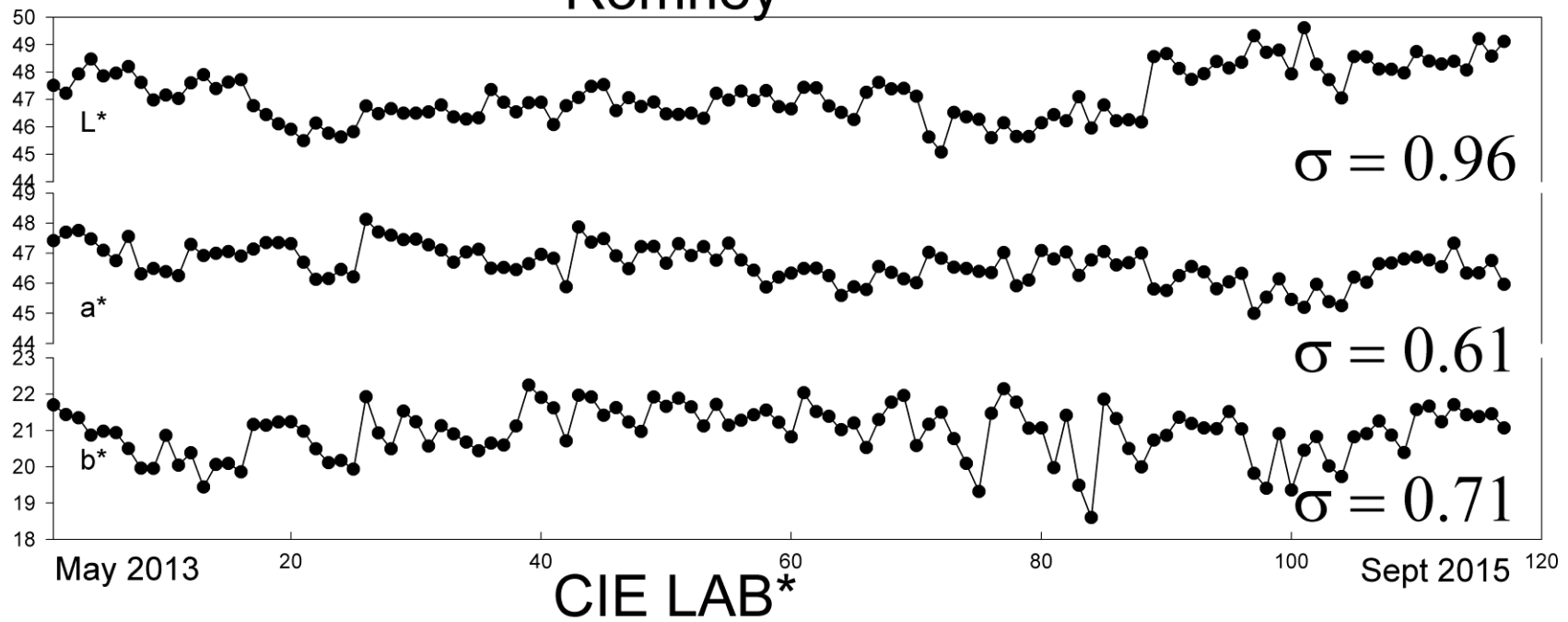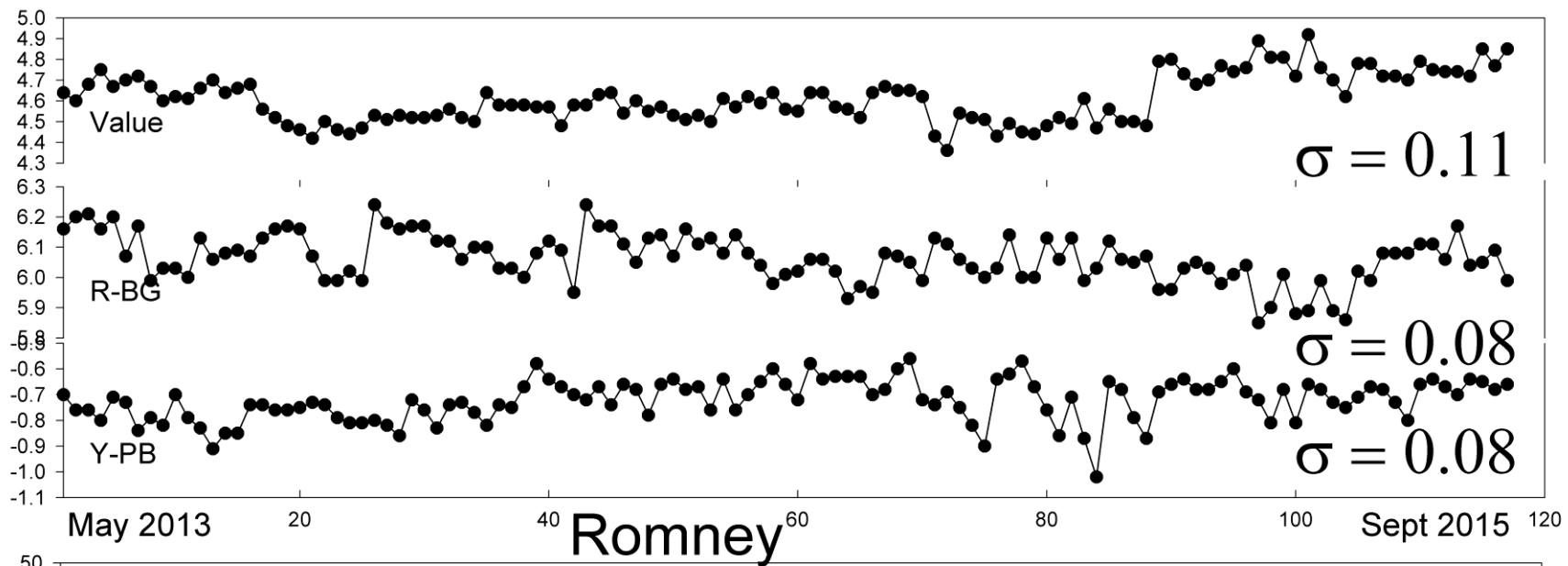Size: Ellipse, 2.0 x 1.5 mm

Fibre Optic
Configuration

Spectrometer and fibre optic used in this study

Typical Reflectance Spectrum

Primary sampling area for parameter determination

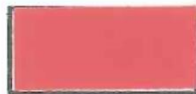Single area reproducibility over a two year period

The TWO & THREE CENT red

Carmine	Place stamp here	Dark Carmine
Rose Carmine		Deep Red
Deep Rose Red	Place stamp here	Red
Orange Red		Pink

Morris Admiral Colour Guide based on the Munsell Colour Chips
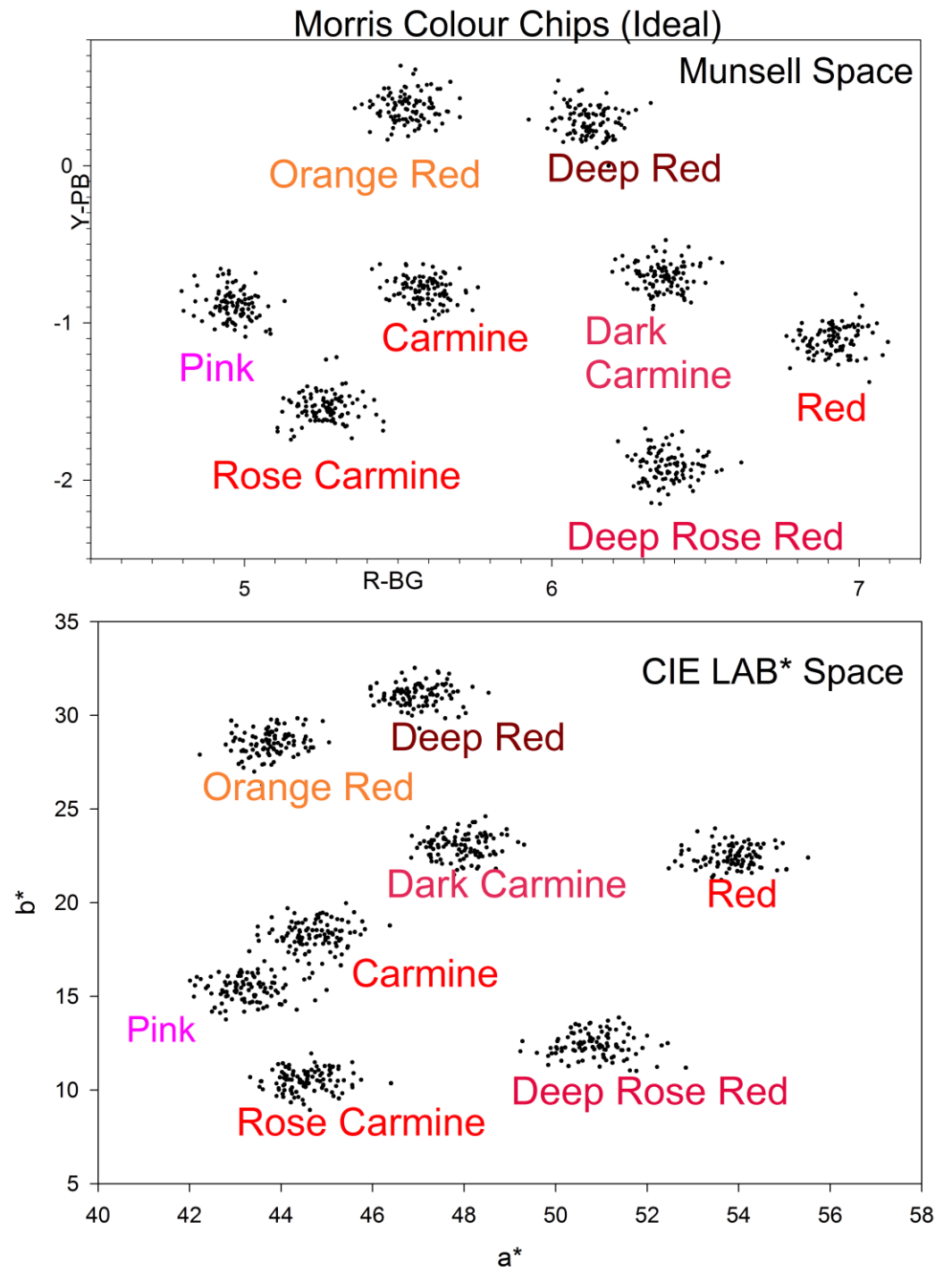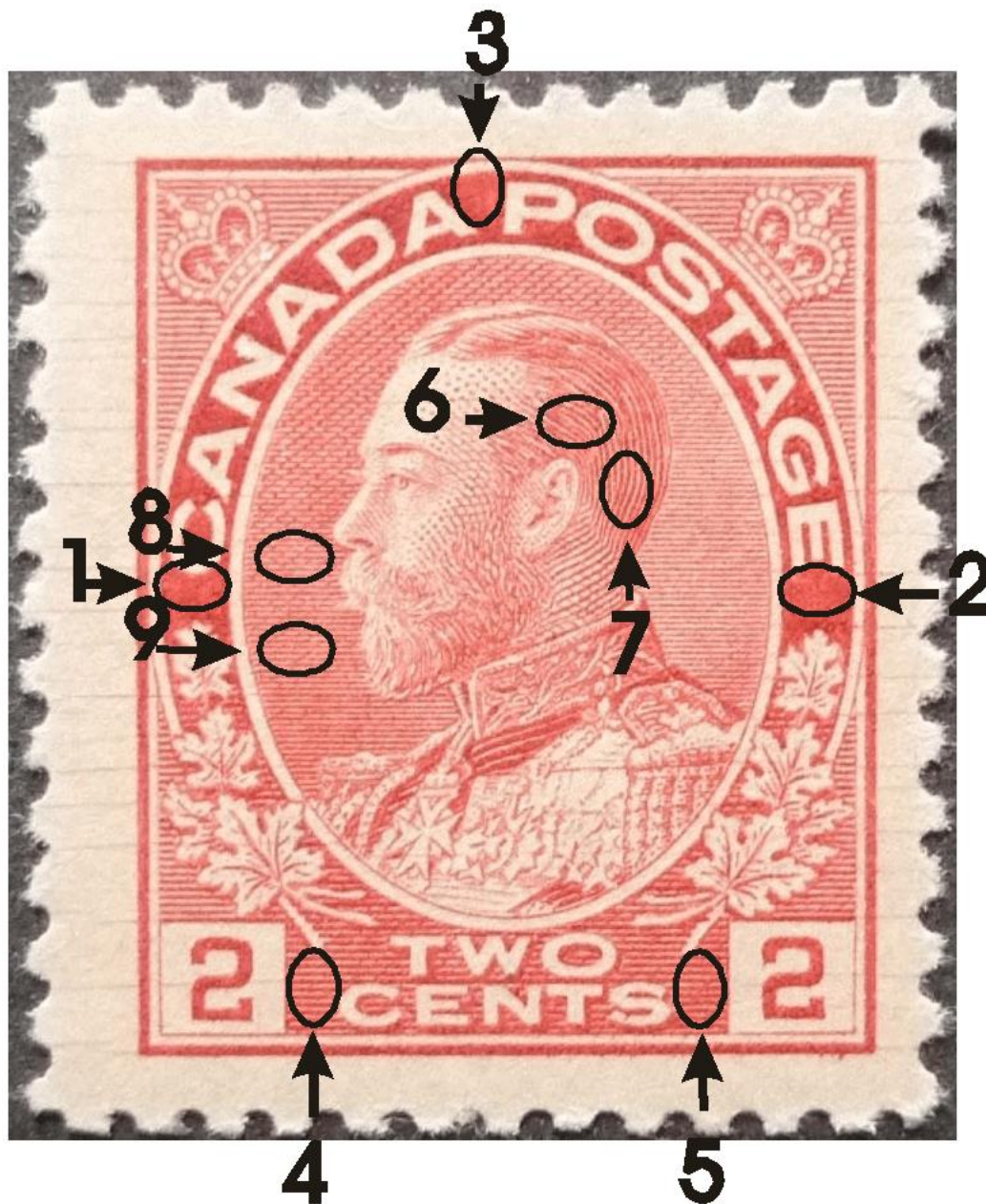
Idealized distribution (single area) based on the Morris Colour Chips and a standard deviation from the quality control standard.

Morris Colour Chips (Ideal)

Munsell Space

Orange Red   Deep Red

Pink   Carmine   Dark Carmine   Red

Rose Carmine   Deep Rose Red

CIE LAB* Space

Orange Red   Deep Red

Pink   Dark Carmine   Red

Carmine

Rose Carmine   Deep Rose Red

The 9 sampling areas

Munsell Conceptual (Romney)

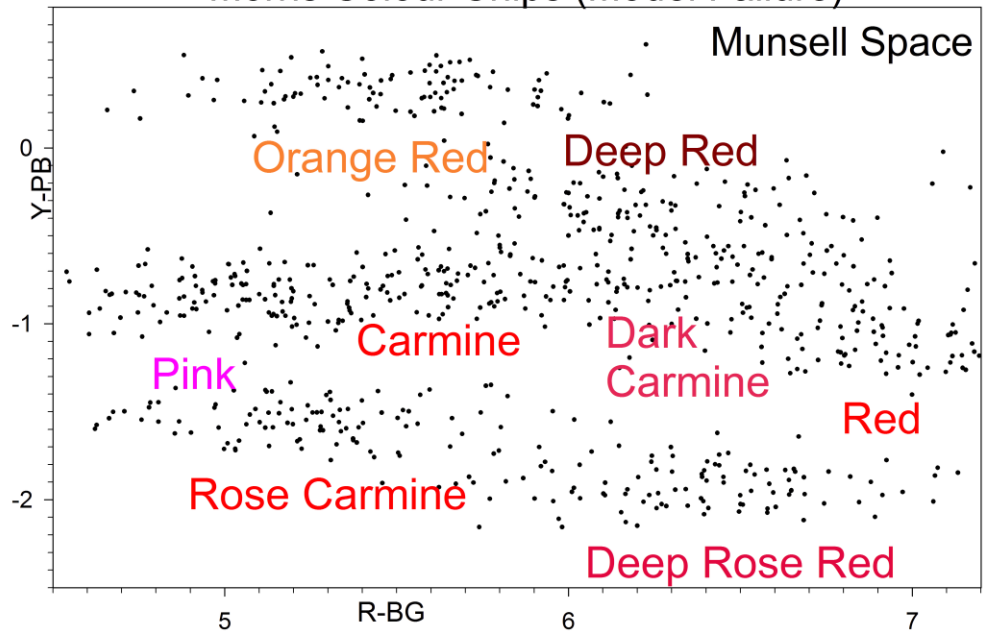| Area	Rose Carmine			Carmine		
	V	R	B	V	R	B
1	5.37	4.95	-0.31	5.37	5.13	-0.34
2	5.13	5.16	-0.47	5.30	5.56	-0.45
3	5.08	4.74	-0.27	5.08	5.19	-0.34
4	5.68	4.74	-0.09	5.52	5.11	-0.26
5	5.21	5.27	-0.36	4.67	6.38	-0.64
6	5.44	5.24	-0.35	4.69	5.85	-0.47
7	5.02	5.68	-0.44	4.79	6.00	-0.51
8	5.79	5.10	-0.32	4.76	6.05	-0.58
9	5.54	5.29	-0.32	4.92	5.95	-0.54
Avg	5.36	5.13	-0.33	5.01	5.69	-0.46
Std	0.27	0.30	0.11	0.32	0.46	0.13
Std (Area 9)	0.08	0.08				

Summary of the variation of the shade parameters determined from the 9 selected stamp areas.
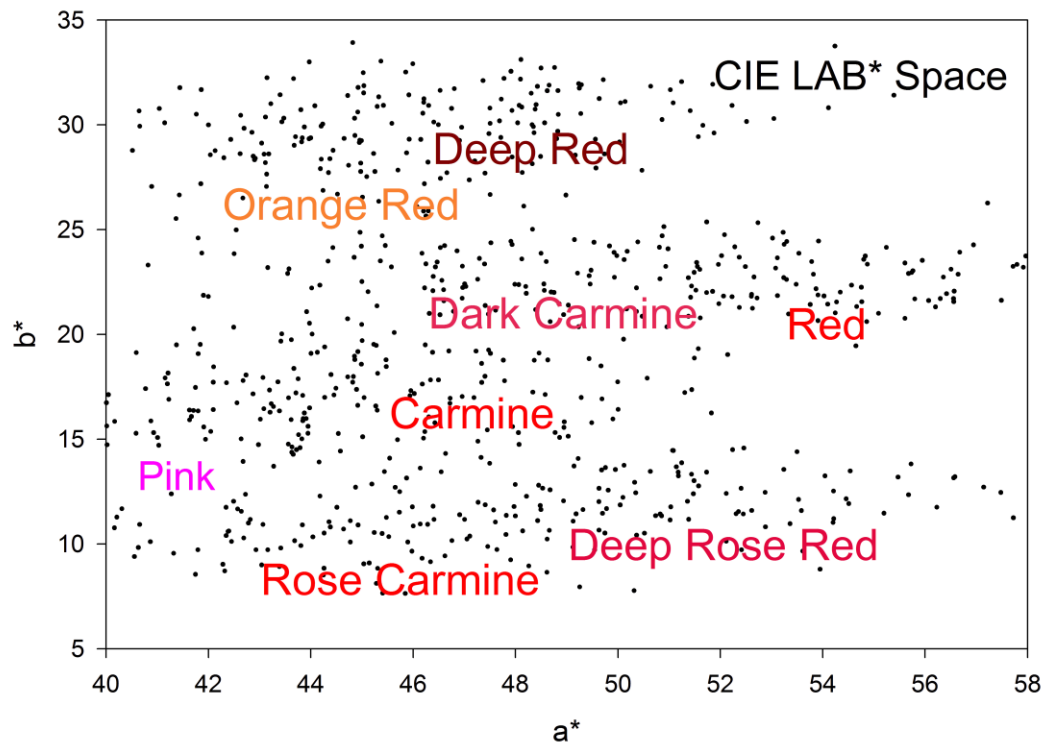
CIE LAB*

Area	Rose Carmine			Carmine		
	L	a	b	L	a	b
1	52.48	36.61	18.61	51.34	32.86	18.30
2	50.48	38.64	18.17	50.99	36.71	19.31
3	49.74	34.76	17.89	48.71	33.21	18.31
4	55.20	34.82	19.61	52.78	32.71	19.01
5	51.41	39.39	19.69	46.10	43.76	21.63
6	53.77	40.02	19.90	46.15	40.88	20.80
7	50.39	43.28	21.20	47.17	42.10	21.22
8	56.88	39.29	19.64	47.02	42.78	21.01
9	54.75	40.42	20.40	48.33	42.01	20.88
Avg	52.79	38.58	19.46	48.73	38.56	20.05
Std	2.49	2.77	1.06	2.43	4.66	1.31
Std(Area 9)	0.61	0.71				

Expected pattern given the standard deviations from measuring the nine stamp areas

Morris Colour Chips (Model Failure)

Munsell Space

Orange Red   Deep Red

Carmine   Dark Carmine

Pink

Red

Rose Carmine

Deep Rose Red

CIE LAB* Space

Deep Red

Orange Red

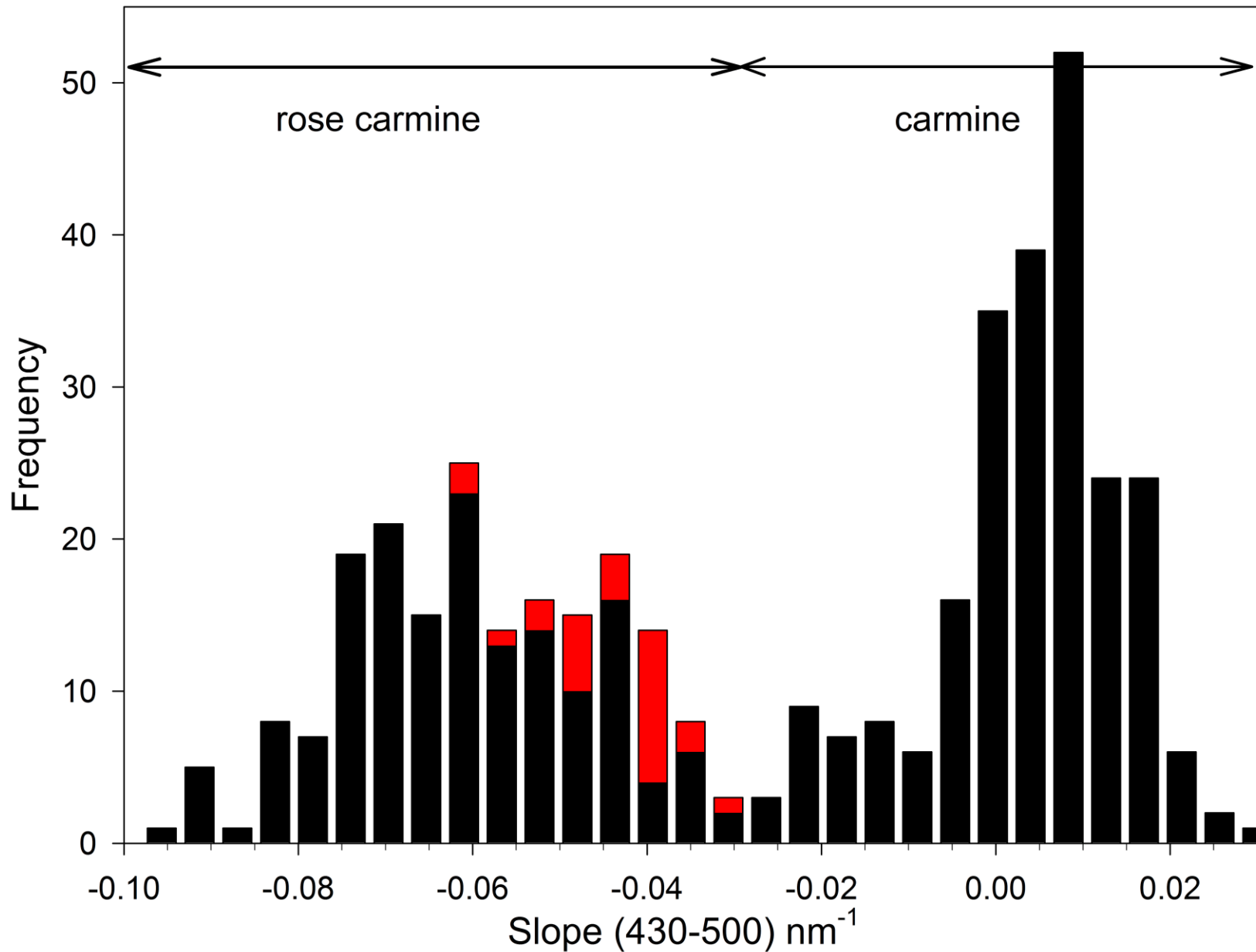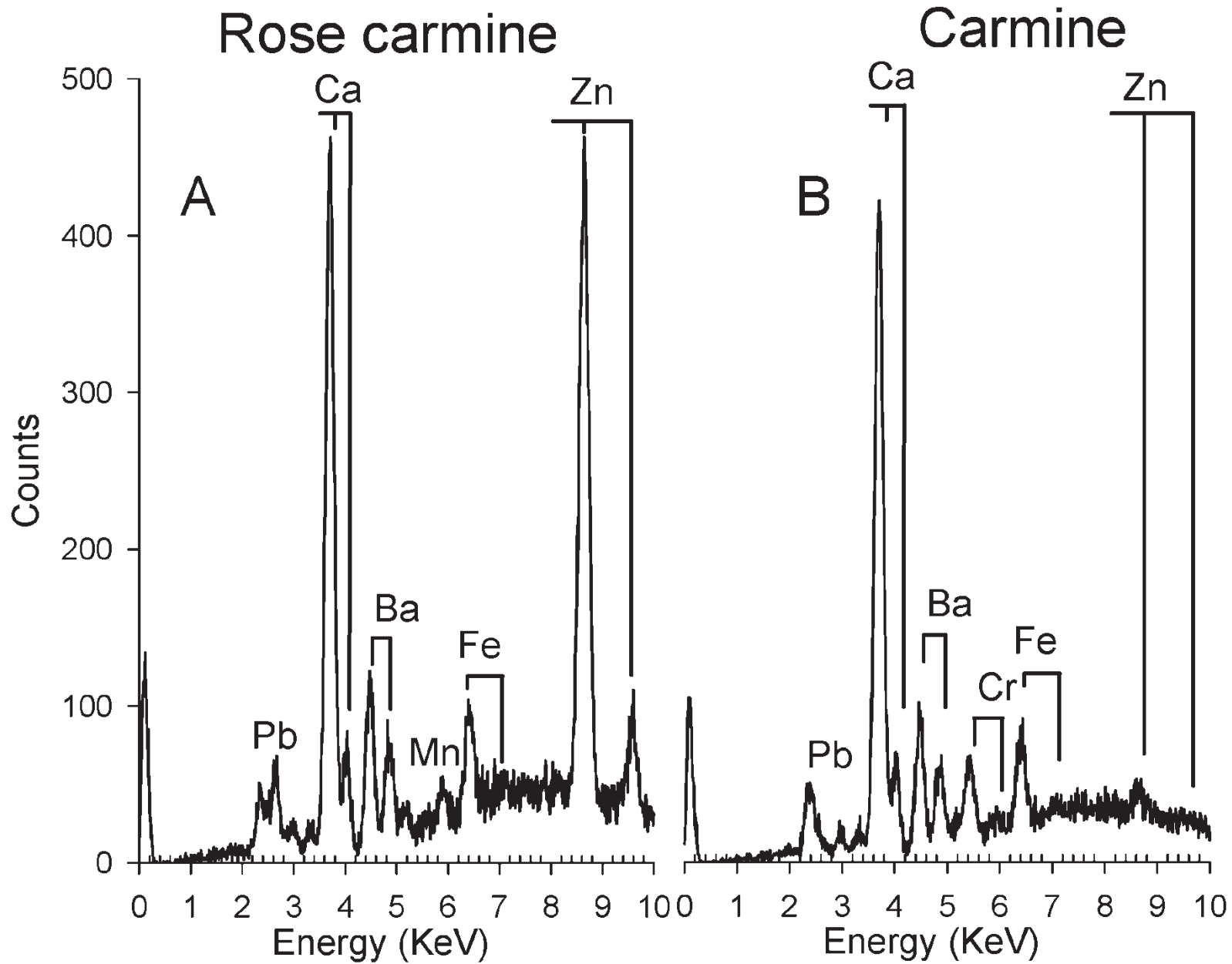Dark Carmine   Red

Carmine

Pink

Deep Rose Red
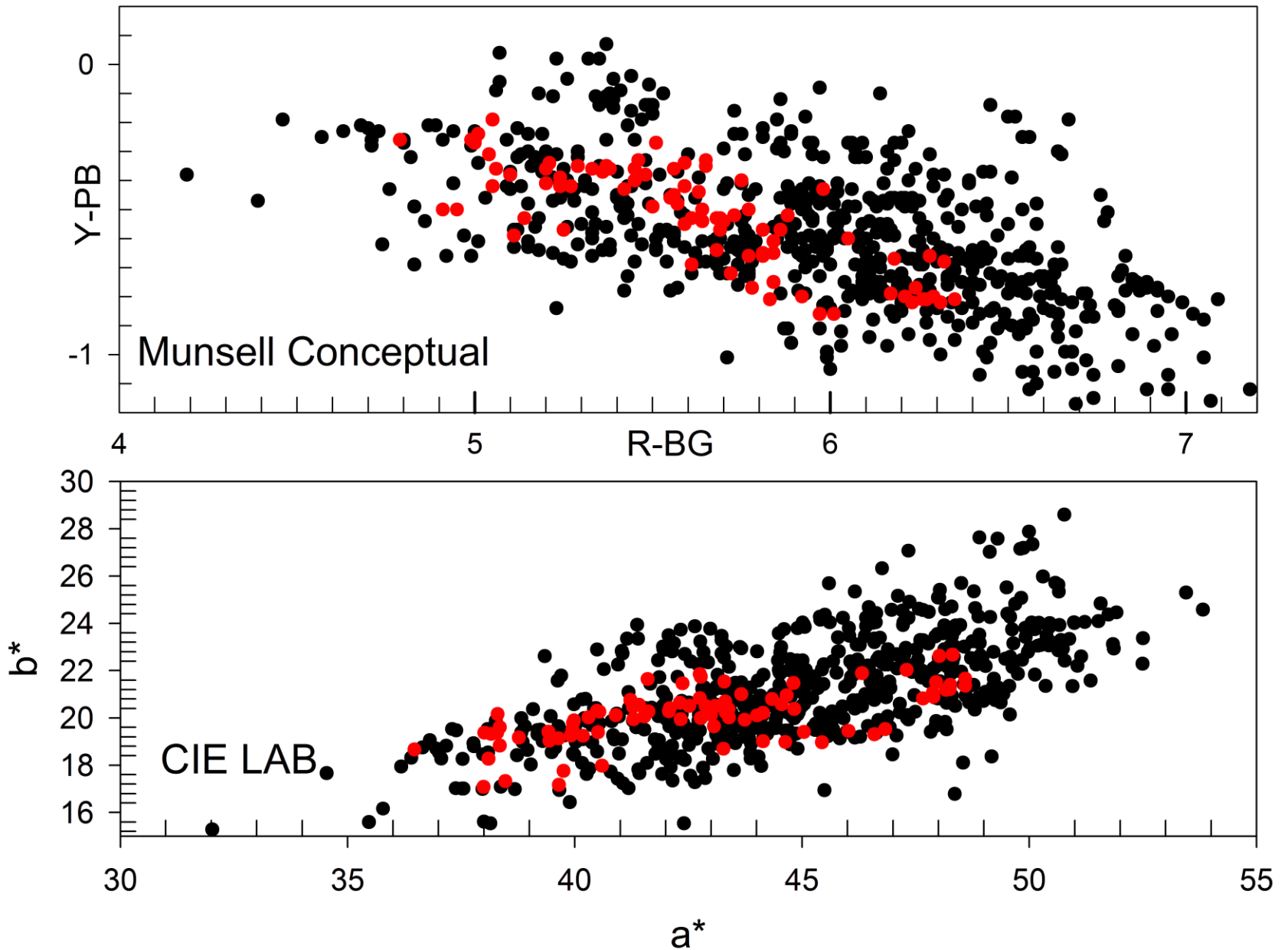
Rose Carmine

Shade distribution with the rose carmine hairline stamps shown in red
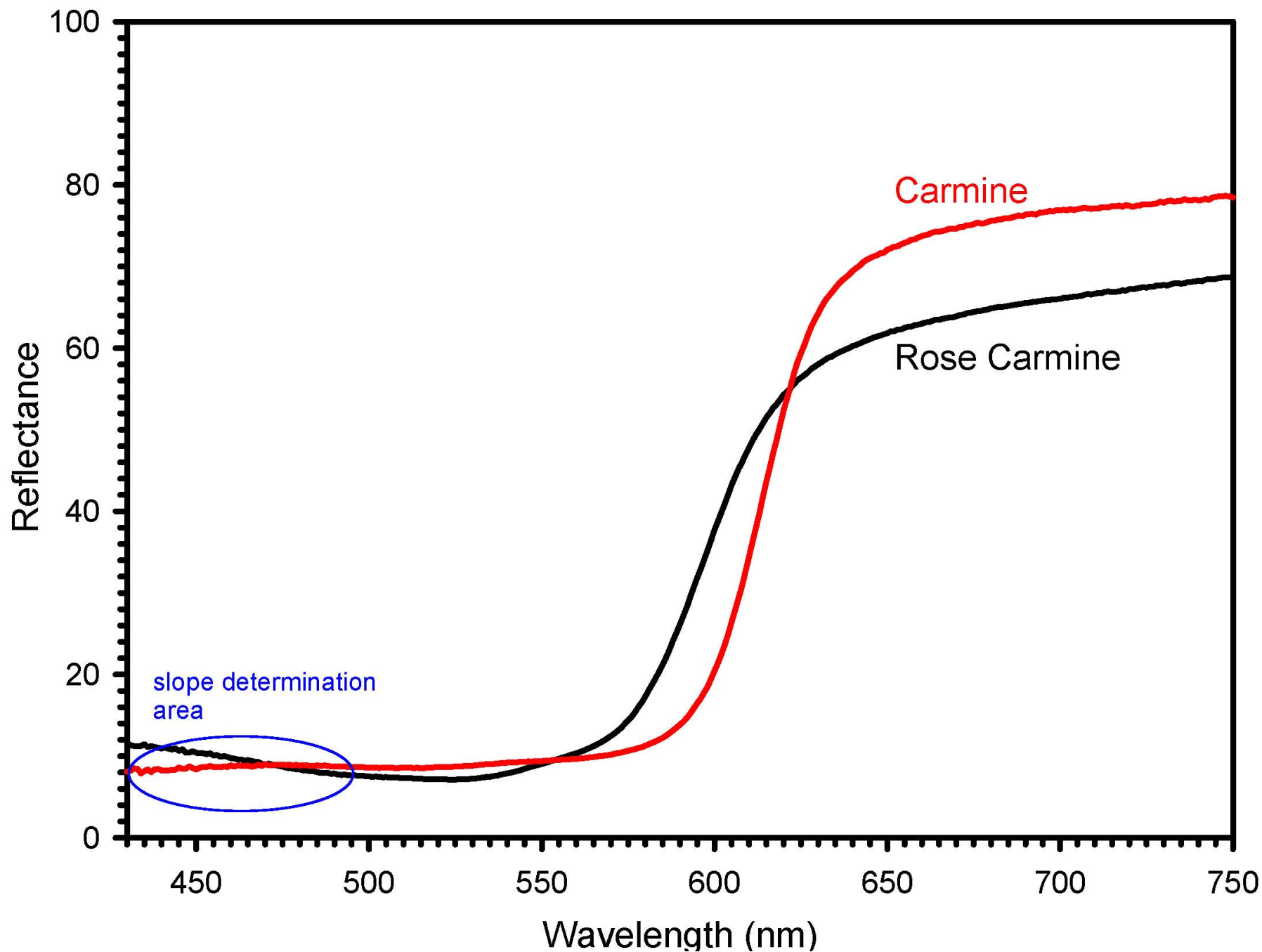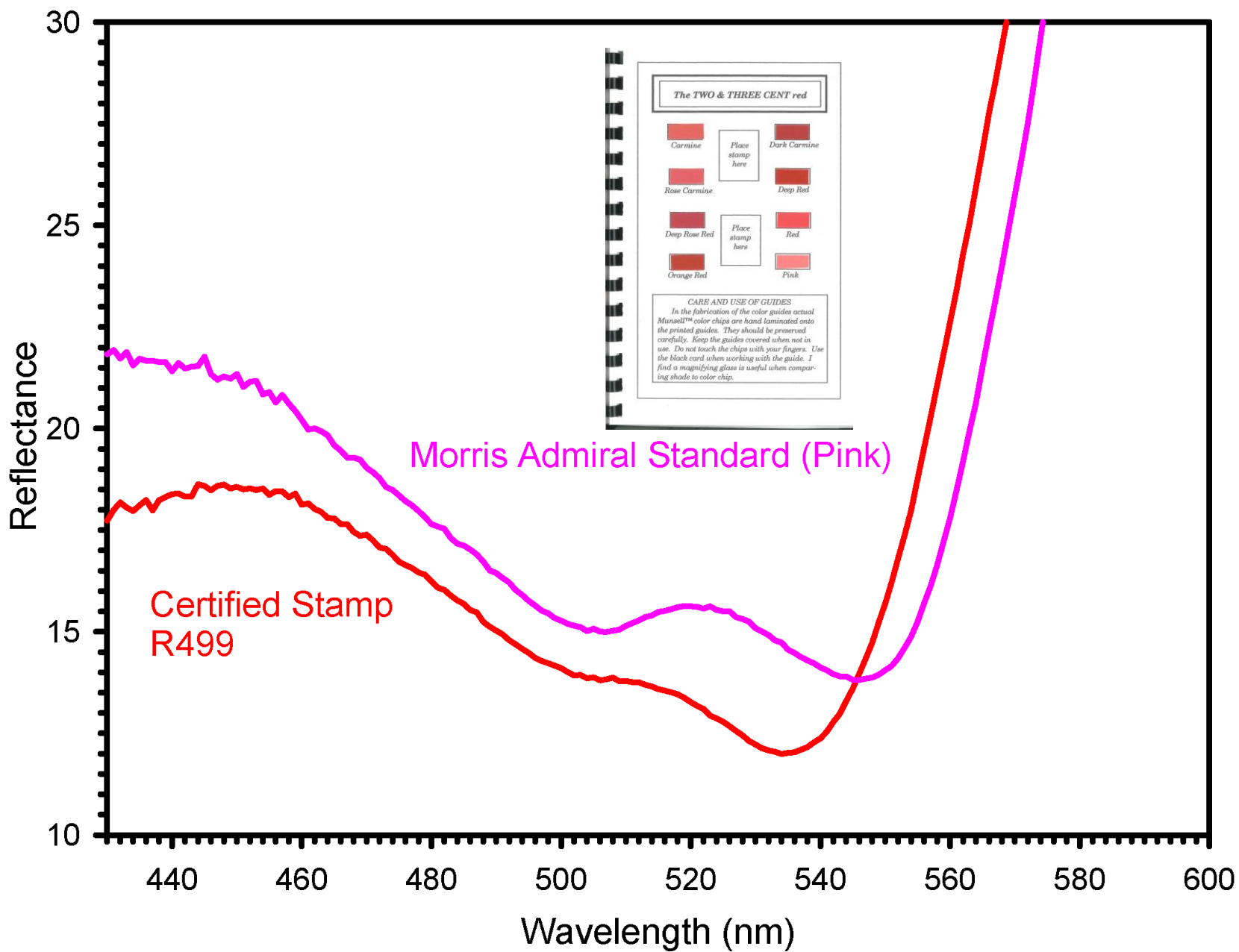
The two major shades and their slope differences at ~450nm

Histogram based on the slope at ~450 nm. Rose carmine (plate 4) hairline stamps shown in red
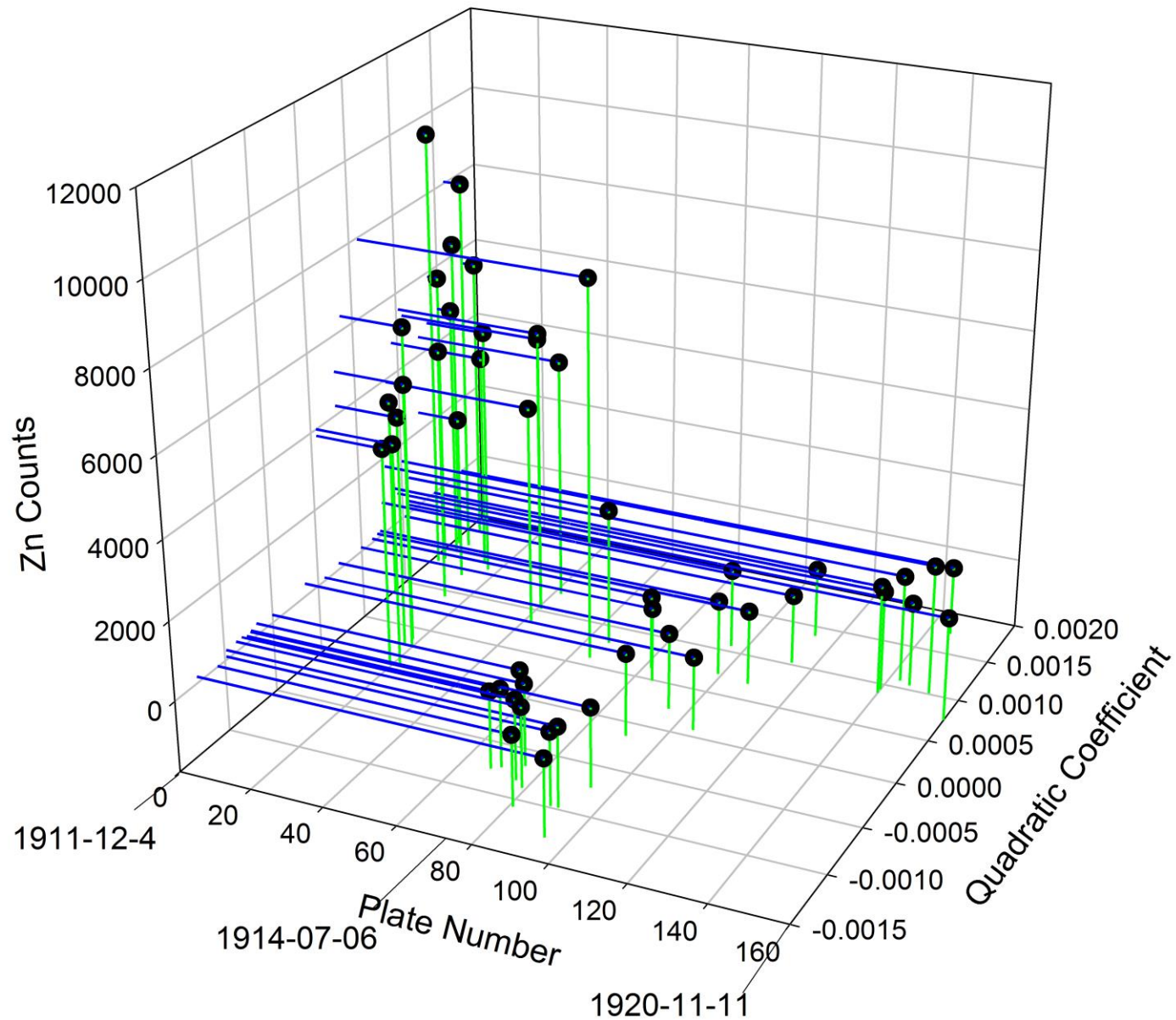
XRF elemental analysis of rose carmine and carmine stamps
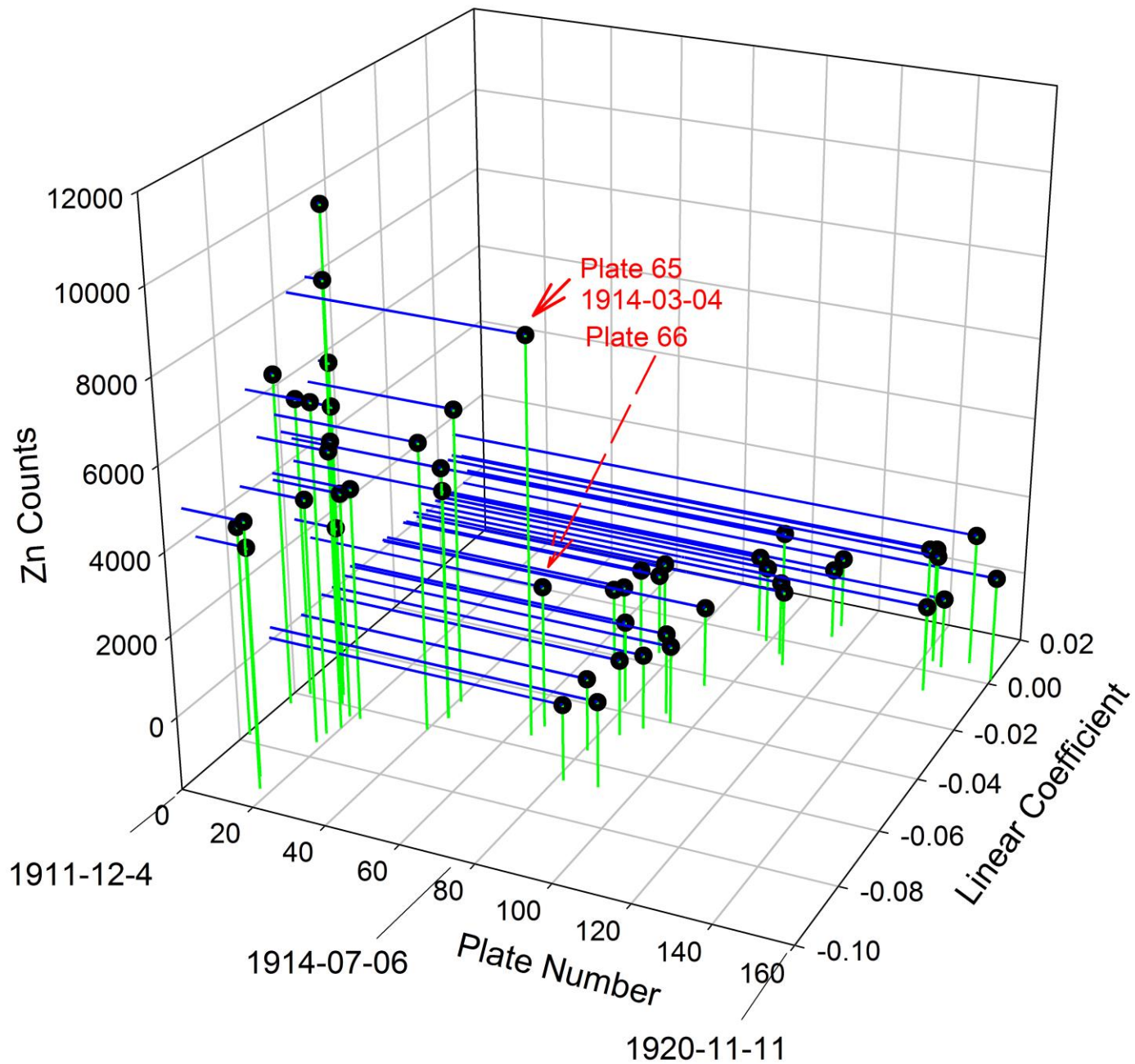
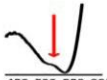**3D plot of time (plate number) (x), slope (y) and zinc content (z)**

The TWO & THREE CENT red

Carmine | Place stamp here | Dark Carmine

Rose Carmine | | Deep Red

Deep Rose Red | Place stamp here | Red

Orange Red | | Pink

CARE AND USE OF GUIDES
In the fabrication of the color guides actual Munsell™ color chips are hand laminated onto the printed guides. They should be preserved carefully. Keep the guides covered when not in use. Do not touch the chips with your fingers. Use the black card when working with the guide. I find a magnifying glass is useful when comparing shade to color chip.

Morris Admiral Standard (Pink)

Certified Stamp R499

Reflectance Spectra of a Morris Admiral pink Muncell chip and a Green Foundation certified pink stamp
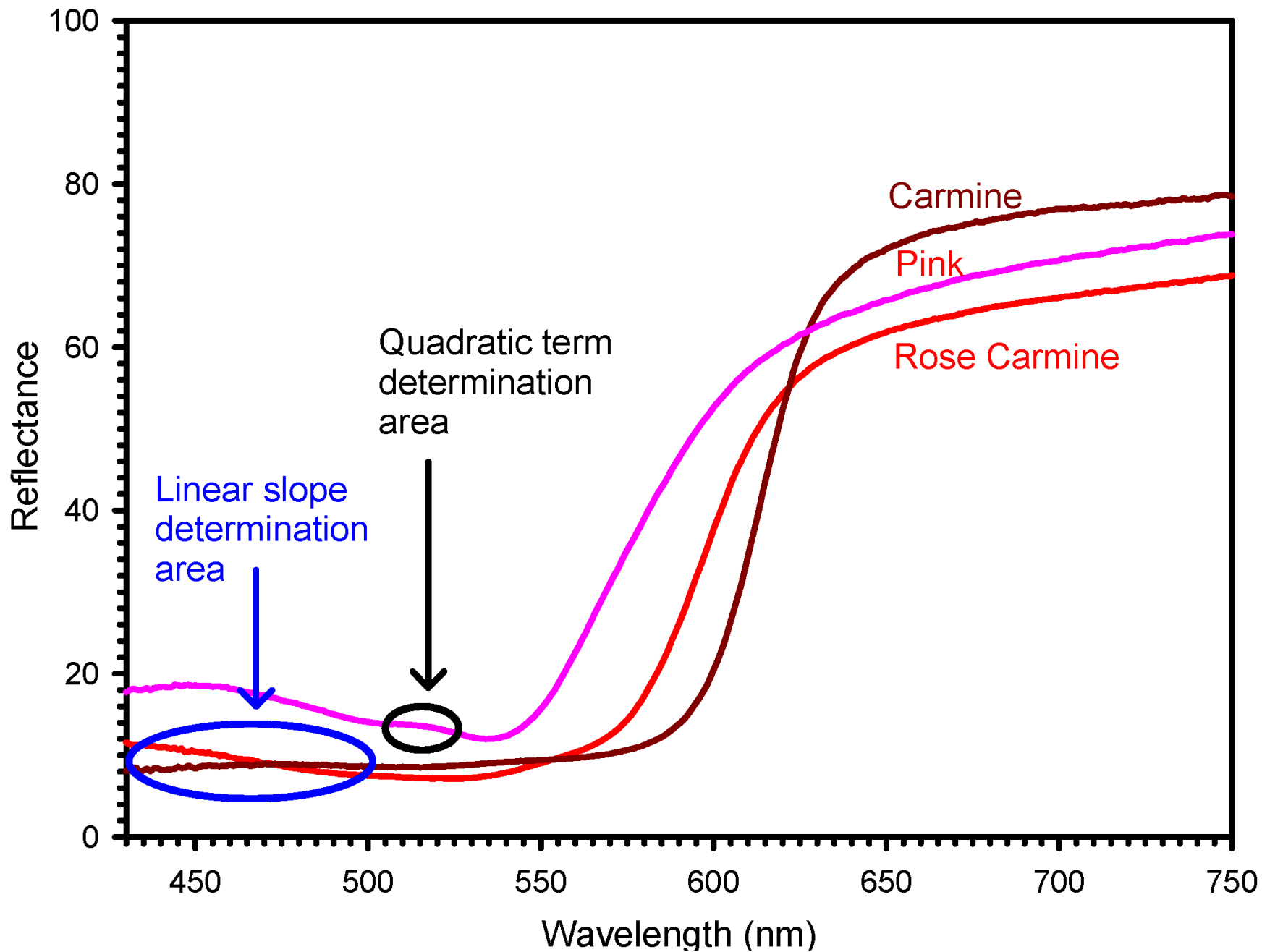
Slope differences in the reflectance spectra of the three major shades

Zn levels and linear slopes for rose carmine, carmine and pink stamps

Variation of the zinc content and quadratic coefficient with plate number (year).

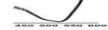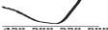| Label	Expertization	Parameters
a	Greene: Jan, 2014 Pink (slightly under inked)	Quad: -0.0037; Lin: -0.0662; Z_n: 50
b	Gratton: July, 2009, Pink; APEX: Apr, 2013, Pink; Sismondo: Nov, 2013, Pink	Quad: -0.0025; Lin: -0.0816; Z_n: 15
c	Greene: May, 2014, Rose Carmine, Aniline Ink Variety Plate 82	Quad: -0.0020; Lin: -0.0627; Z_n: 105
d	Greene: Oct, 2013, rose car	Quad: -0.0003; Lin: -0.0166; Z_n: 114
e	Greene: Apr, 2014 rose car, aniline ink. Plate 91	Quad: -0.0002; Lin: -.0707; Z_n: 30
f	Greene: Dec, 2012, Pink; Apex: Apr, 2013, rose car; Sismondo: Nov, 2013, car	Quad: +0.0014; Lin: -0.0471; Z_n: 6010
g	Greene: Mar, 2014, Pink	Quad: +0.0017; Lin: -0.0782; Z_n: 2988
h	Greene: June, 2013, Pink; C.E.P.L: Sept, 2012, Pink	Quad: +0.0013; Lin: -0.0814; Z_n: 3436
i	Greene: Nov, 2012, rose car	Quad: +0.009; Lin: -0.0619; Z_n: 7446
j	Greene: Oct, 1999, Pink Plate 1	Quad: +0.001; Lin: -0.0749; Z_n: 3429
k	Greene: Oct, 2013, Pink	Quad: +0.0011; Lin: -0.0815; Z_n: 4864

Summary of expertization certificates and parameter values

Acknowledgments

I am pleased to acknowledge the help and encouragement offered by:

John Barwis, president and senior fellow IAP. He was instrumental in getting this study started through his critical evaluation of my earlier investigation of the hairline variety.

Tom Lera of the National Postal Museum. His patience and help in obtaining the XRF and FTIR data on the plate blocks is most appreciated.

Fred Baumann of the American Philatelic Research Library (APRL) who supplied very valuable and complete references to the available literature on the aniline ink problem.

I am grateful to the Institute of Analytical Philately (IAP) for a generous grant to obtain the spectra and to present this work.

"Wide variations in shade can be obtained with the same ink if varying thicknesses of ink are used. A scarlet red, for example, may be converted into a weak pink tint solely by using insufficient ink during the printing of the sheets. "

Postage Stamps in the Making by F.J. Melville (1916). Rewritten and Completed by John Easton (1949).