I found paintings using a complementary color scheme all the way to 1400-1500, which to me was really surprising given that the traditional color wheel and the color pairing where first studied until the seventeen century. The first two examples I found were from Lorenzo Monaco (Piero di Giovanni) in the early 1400's.



1

¹ Last Judgment in an Initial C, ca. 1406–7. Lorenzo Monaco (Piero di Giovanni)



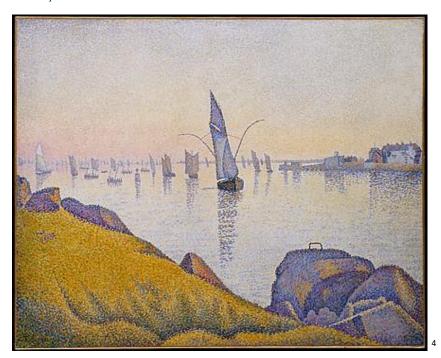
I also found a painting from an unknown author in 1500's from the Netherlands, who mostly used orange and blue hues.



² The Nativity, ca. 1406–10. Lorenzo Monaco (Piero di Giovanni)

³ The Triumph of Fame, circa 1502–4. Netherlandish, probably Brussels

Paul Signac also worked with a complementary scheme in a few of his paintings from 1889, like the ones shown below:





⁴ Evening Calm, Concarneau, Opus 220 (Allegro Maestoso),1889. Paul Signac

⁵ The Jetty at Cassis, Opus 198,1889. Paul Signac

And lastly, I found these examples by Henri Matisse while visiting the MET this past Friday:



⁶ Laurette in a Green Robe, 1916. Henri Matisse



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8

⁷ Lilacs. Henri Matisse. 1914

⁸ Marguerite with Black Velvet Ribbon. 1916