PG36 PG10 PG9 PG8 PG7 PB60 PB16 PB15:6 PB15:4 PB15:3 PB15:2 PB15:1 PB15 PV37 PV36 PV32 PV27 PV23 PV19 PV5 PV3

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Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection

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ABSTRACT

Some 170 organic pigments relevant to artist's paints have been collected from historic collections and modern manufacturers. The number includes multiples of the same pigment from different sources and comprises 118 different color indices (C.I.). All of them have been analysed with FTIR spectroscopy and 125 pigments (93 different C.I. No.s) of particular relevance to artist's paints have been characterised with Raman spectroscopy so far. The pigment collection encompasses the following pigment classes and subgroups: monoazo pigments represented by acetoacetic arylide yellow (hansa yellow), β-naphthol, BON, naphthol AS and benzimidazolone; disazo pigments with disazo condensation, diarylide, bisacetoacetarylide, pyrazolone; azo-azomethinmetal complex pigments; non-azo, polycyclic pigments such as phthalocyanines, diketopyrrolo-pyrroles (DPP), perylenes and perinones, quinacridones, isoindolinones, polycarbocyclic anthraquinones and dioxanines. The selection of references was based on availability (historic collections) and current use in 16 acrylic, alkyd and oil-based artist's paints, and it covers pigment colors PY yellow (27 C.I. No.s), PR red (38), PO orange (9), PB blue (8), PV violet (6), PG green (3) and PBr brown (2). Besides peak tables and spectra patterns, flow charts based on color, pigment class, group and individual color index are presented to help identification of unknowns and mixed paint samples. While Raman could isolate all different C.I. numbers, multiple references of the same C.I. from different sources could not be distinguished.

Acrylic, Oil and Alkyd Artist's paint		Schmincke Primacryl	Schmincke Akademie Acryl	Talens Rembrandt Acryl	Talens Van Gogh Acryl	Winsor & Newton Artist's Acrylic Colour	Winsor & Newton Galerie Acrylic Colour	Golden Acrylics	Schmincke Mussini Oil / Resin	Schmincke Norma Oil prof.	Talens Rembrandt Oil	Talens Van Gogh Oil	Talens Amsterdam Oil	Talens Van Gogh H2O	Winsor & Newton Artist's Oil Colour	Winsor & Newton Oil Colour	Winsor & Newton Gryffin Alkyd	
	1 pigment (single pigment colour)	55	24	38	18	62	34	79	59	34	58	32	17	16	82	21	35	
	2 pigments	15	19	21	16	11	14	6	18	22	35	24	9	18	27	17	10	
	3 pigments	14	14	15	6	1	10	2	17	13	30	10	9	5	9	7	5	
	4 pigments		2	1						8	11							
	5 pigments		1							1	1							
	Colour	Colour Index Generic Name																Pigment combinations
PY 3	Monoazo, Acetoacetarylide	**PY 3**	***PY 3***	***PY 3***	**PY 3**	**PY 3**	**PY 3**	**PY 3**	**PY 3**	**PY 3**		***PY 3***	***PY 3***	***PY 3***	**PY 3**	**PY 3**	**PY3**	PW4,5,7, **PY**53,**74,150,154**, **PO67**, **PB15,15:3**, **PG7**,19,**36**
PY 53	Cadmium zinc sulfide	PY 35		PY 35		PY 35	PY 35	PY 35	PY 35	PY 35	PY 35	PY 35			PY 35		PY 35	PW6,21, PO20, **PB15:3**, PG18
PY 42	Synthetic iron oxide	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	PY 42	*PY 42*	PW4,6, **PY**43,**74,138,153,154,155**,184, **PO43**, PR101,**188**, PV19, PB15,15:6,27, PG7,17,36, PBr7,24, PBk6,7,10,11,19
PY 43	Natural iron oxide					*PY 43*		PY 43	PY 43	PY 43		PY 43	*PY 43*		PY 43	*PY 43*	PY 43	PY42, PR57:1,101, **PG7**, **PB15,15:4**, PBr 6,7, PBk11
PY 47	Lead titanate														*PY 47*			PW6, **PG7**
PY 53	Nickel antimony titanate, Rutile	PY 53	PY 53	*PY 53*	*PY 53*			PY 53	*PY 53*	*PY 53*					PY 53			PW4,6, **PY3,153,154,155**, PG19, PBr24
PY 65	Monoazo, Acetoacetarylide						**PY 65**								**PY 65**	**PY 65**		PW6, **PY74,138**, **PO73**, **PR9**, **PB**27,**60**, PBr24
PY 73	Monoazo, Acetoacetarylide						**PY 73**	**PY 73**										
PY 74	Monoazo, Acetoacetarylide	***PY 74***	**PY 74**	**PY 74**	***PY 74***	**PY 74**	**PY 74**	**PY 74**	***PY 74***		***PY 74***	***PY 74***	***PY 74***		**PY 74**	**PY 74**	**PY 74**	PW5,6,7, **PY3**,42,**65,154**, **PO43,62**, **PB15,15:1**, **PG7,36**
PY 83	Diazo, Diarylide		**PY 83**			**PY 83**	***PY 83***	**PY 83**		***PY 83***								**PY74,138**, **PB15**,27,**60**, PBr24
PY 100	Monoazo, Tartrazine lake															***PY 100***		**PG12**
PY 109	Polycyclic, Isoindoline										***PY 109***							PW4, PG36
PY 110	Polycyclic, Isoindoline			***PY 110***						***PY 110***	**PY 110**	**PY 110**		**PY 110**	***PY 110***			**PR177,264**, **PB15**, **PG7**, PBk6
PY 119	Zinc magnesium ferrite, Spinel	*PY 119*	*PY 119*															PW 6
PY 128	Disazo, Disazo condensation			**PY 128**	***PY 128***	**PY 128**					**PY 128**	***PY 128***			**PY 128**			PG 7
PY 129	Azomethine copper complex						**PY 129**		***PY 129***		**PY 129**			***PY 129***	**PY 129**		***PY 129***	PG7, PBk7
PY 138	Quinophthalone														***PY 138***			PW4,6, **PY**42,**83,153,154**, **PO62**, **PR188**, **PG7**, PB27
PY 139	Polycyclic, Isoindoline														***PY 139***		**PY 139**	PR101
PY 150	Azo, Nickel complex	**PY 150**					**PY 150**	**PY 150**	**PY 150**	***PY 150***	**PY 150**				**PY 150**			**PY3**, **PO48**, **PB60**, **PG36**, PBr7
PY 153	Nickel Dioxine, Ni-complex	**PY 153**							**PY 153**	**PY 153**								PW6, **PY**42,53,**138,154**, PR101, **PG7**, BBr24
PY 154	Monoazo, Benzimidazolone	**PY 154**								***PY 154***	**PY 154**	***PY 154***	***PY 154***	***PY 154***				PW4,5,6, **PY3**,42,27,53,**74,138,153**, **PO43**, **PG7**, PBr24
PY 155	Disazo, Bisacetoacetarylide	**PY 155**							**PY 155**									PW4,6, PY42,53, PV15, PG17
PY 184	Bismuth vanadate	PY 184				PY 184			PY 184	*PY 184*	PY 184				PY 184			PW4, PY42, **PO67**, **PG7**,18,38,50

Synthetic organic pigment
Bold Generic name: Synthetic organic pigment
Regular Generic name: Not synth. organic pigment
Italic Pigment only used in combination, not as a single pigment

Information from colour chart declarations 2008

Pigments in Artist's paint total: 120 pigments
Synthetic organic pigments: 71 pigments
Inorganic pigments: 49 pigments

Tab. 1 This is an excerpt of table 1 of the full text article. The aim of this table was to deliver a survey of pigments and pigment combinations declared in current artist's paint products by Schmincke, Talens and Winsor & Newton in 2008. It highlights the growing importance of synthetic organic pigments in such paint products and gives a first grasp of the pigments that need to be included in such a reference collection. Further differentiation was made on pigments used only in combination with other pigments.

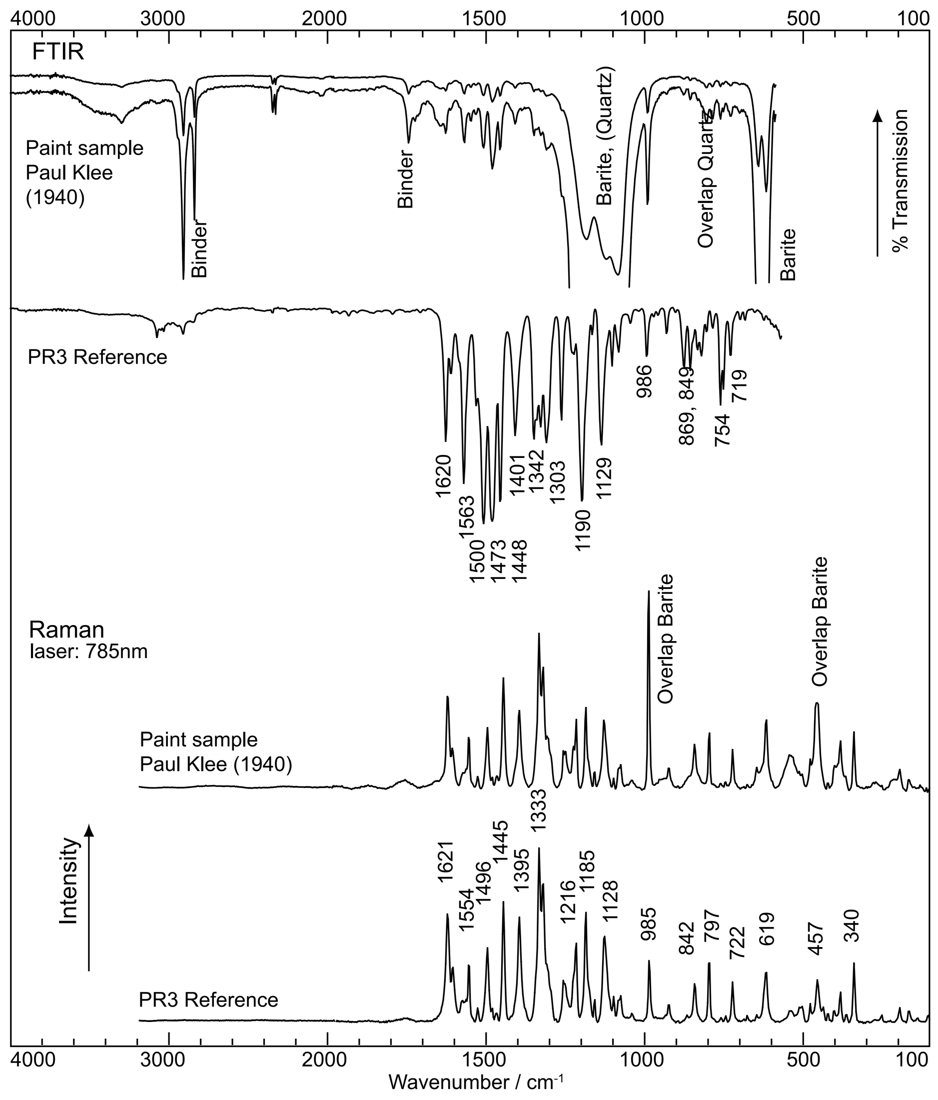

Fig. 1 Comparison of FTIR and Raman data of a red paint sample taken from the artwork „Glass-Fassade", 1940, by Paul Klee. This example demonstrates the different signal contributions of pigment, substrate, filler and binding media - and intensity ratios thereof. While FTIR is able to record all components of the paint, it suffers from interferences and the low intensity of the synthetic organic pigment, which is readily identified with Raman.

Introduction The use of synthetic organic pigments in artist's paint products has dramatically increased and is now well established. In the early 20th century, there has been an enormous expansion of synthetic pigment developments, with examples where new organic pigments were found in artwork shortly after their introduction to the market. While organic pigment usage in artist's paint products has been conservative for a long time, a survey of current (2008) artist's paint products by Schmincke, Royal Talens and Winsor & Newton has revealed that almost 60% of pigments within those 16 product palettes are organic. Furthermore, the combination of pigments to achieve a specific hue varies largely across the products. This, of course, generates new analytical challenges for forensic and art technological laboratories.

Methods Based on current artist's paint brochures (**Tab. 1**), literature on the early 20th century pigment developments, early colour swatches and artist's correspondence, as well as sampling of historic pigment collections, a comprehensive collection of reference material has been assembled. These materials were systematically recorded with all relevant information available (CI Name, CI Number, Product Name, Pigment Class, Group, Manufacturer, Source Collection, Year of discovery,...). FTIR and Raman spectra were acquired (**Tab. 2**) to be compiled in a reference database and generate tools for the identification of unknowns taken from real artwork.

Results and discussion FTIR and Raman spectra from pure reference compounds and mixed paint from real artwork were compared and the results clearly emphasize the complementary nature of FTIR and Raman (**Fig. 1**), recommending FTIR to identify binders, ageing products, filler ratios and many pigments in an efficient survey, while Raman delivers great performance when it comes to identifying both inorganic and synthetic organic pigments, as well as mixtures thereof. Raman has proven high reproducibility to within 1 wavenumber, allowing separation of different C.I. numbers using a flowchart (**Fig. 2**). Distinction of identical C.I. numbers from different manufacturers or batches, however, is not feasible (**Fig. 3**). Variability of baselines, a nuisance for automatic matching algorithms, have shown to potentially hold additional information on chemical groups, ageing or impurities (trace pigments mixed in to match a specific hue). Distinction of crystal modifications such as α-, β, and ε-type of phthalocyanines is feasible with Raman, though care needs to be taken to avoid artefacts such as peak shifting induced by excessive laserpower, causing (unnoticed) alteration of the pigment upon interaction with the laserbeam. The phthalocyanine flowchart presented in 2009 had to be significantly revised and was presented as a *corrigendum* in Scherrer 2011 *(RAA2011, Parma, IT)*.

Conclusion Raman spectroscopy is a powerful tool to identify organic pigments in artist's paints, yet identification of unknowns stands and falls with a comprehensive reference spectra collection, preferentially generated with 785nm excitation.

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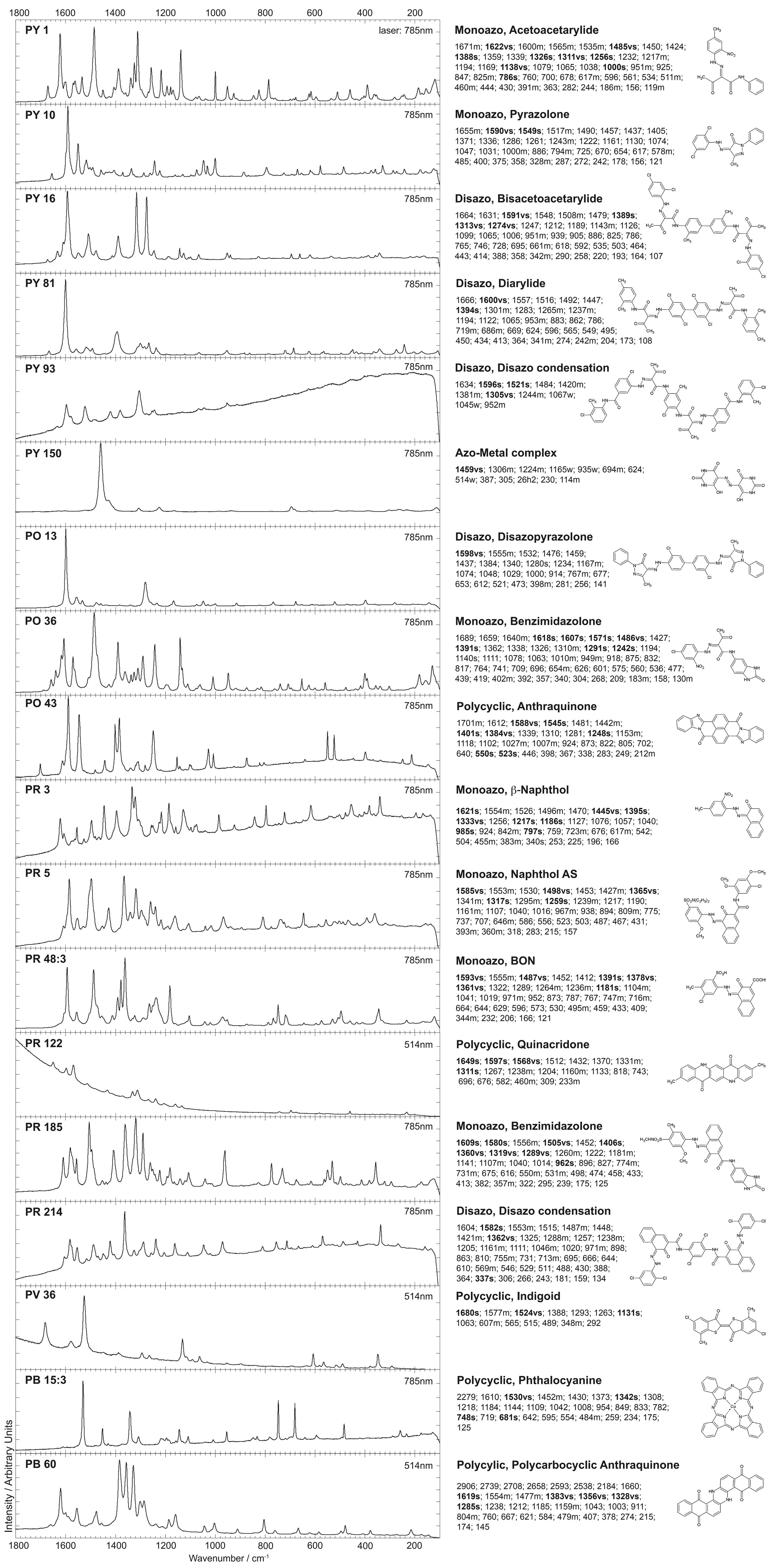


Tab. 2 Example Raman reference spectra including peak tables and molecular structures across the pigment classes and groups comprised by this collection. The general approach was to use 785nm excitation. Other wavelengths available came into action where 785nm could not deliver a suitable response. The main reason for choosing this strategy is the fact that the use of 514 or 633nm excitation on real paint samples is very often strongly limited by fluorescence contribution of binder or ageing products.

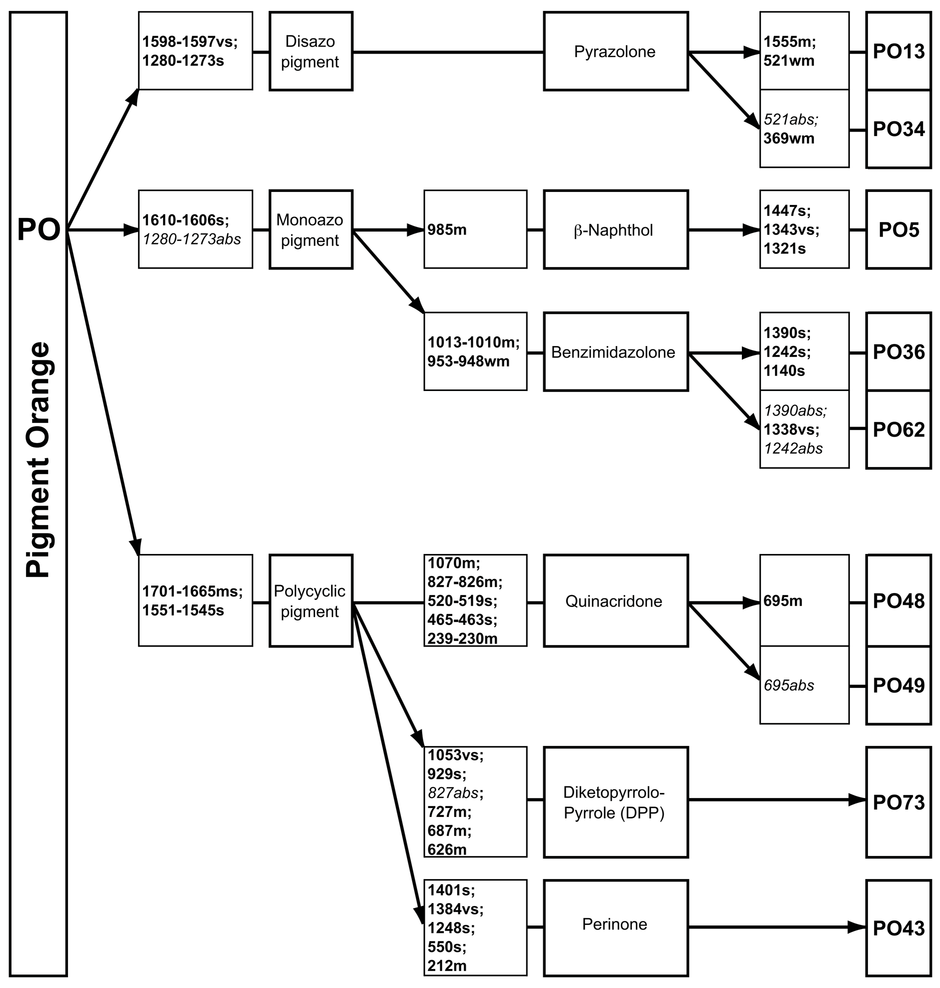
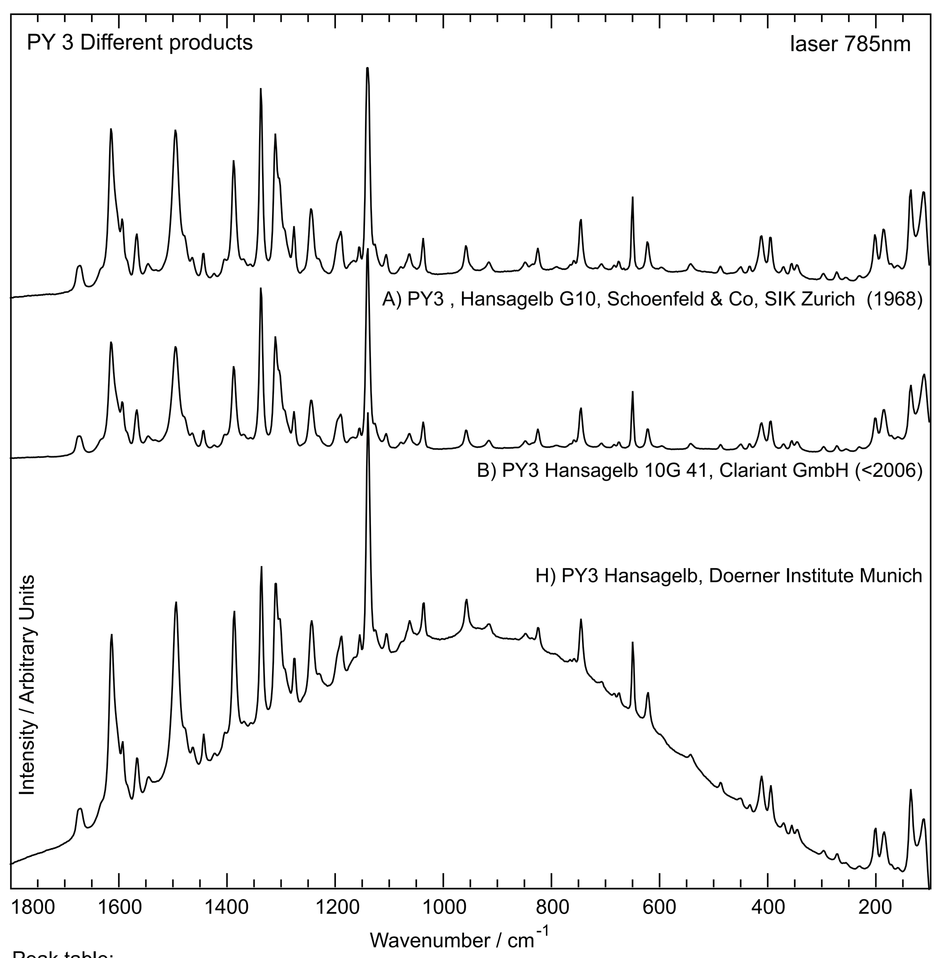


Fig. 2 Example of a systematic flowchart applicable to the dataset of orange pigments. Due to the multiple peaks of organic pigments, identification using a simple peak table is not feasible. The use of systematic flowcharts, however, is always limited by the dataset included. With the growing number of pigments, spectral database systems using matching algorithms is the most feasible strategy.



Peak table:
A) 1614vs; 1567m; 1495vs; 1387s; 1337vs; 1310vs; 1244m; 1192m; 1140vs; 746m; 650s; 622m; 412m; 395m; 202m; 185m

Fig. 3 Comparing Raman spectra of pigment yellow PY3 of variable age and different sources, analysed on the same instrument on separate days. The peak precision is within 1 wavenumber for all peaks. One significant difference, though, is the curved fluorescence background observed on historic reference samples. This example hints at potential information hidden in the baseline.

PY1 PY1:1 PY2 PY3 PY5 PY6 PY10 PY16 PY65 PY73 PY74 PY81 PY83 PY93 PY95 PY97 PY109 PY111 PY120 PY129 PY139 PY150 PY151 PY154 PY155 PY175 PY181 PY194

PBr25 PBr23 PR264 PR255 PR254 PR242 PR214 PR188 PR187 PR185 PR179 PR170 PR166 PR149 PR146 PR144 PR122 PR112 PR83:1 PR68 PR57:1 PR57 PR53:1 PR53 PR49:2 PR49:1 PR49 PR48:3

PO5 PO13 PO34 PO36 PO43 PO48 PO49 PO62 PO73 PR2 PR3 PR4 PR5 PR7 PR8 PR9 PR10 PR11 PR12 PR16 PR18