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SEPARATION AND IDENTIFICATION OF SYNTHETIC ORGANIC PIGMENTS IN ARTISTS' PAINTS BY THIN-LAYER CHROMATOGRAPHY

G A MILOVANOVIĆ*, M RISTIĆ-ŠOLAJIĆ and T J JANJIĆ

Institute of Chemistry, Faculty of Sciences, University of Beograd P O Box 550, 11001 Beograd (Yugoslavia)

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SUMMARY

A thin-layer chromatographic method on silica gel is described for the separation and identification of synthetic organic pigments in artists' oil and acrylic paints. Six solvent systems are proposed, and it is established that, except in the case of paints containing phthalocyanine pigments, the presence of the binding medium has no effect on the separations and R_F values obtained. For the removal of binding medium from phthalocyanine paints, a multiple extraction with suitable solvents is suggested.

INTRODUCTION

Knowledge of the composition of paints is of great importance for the solution of the growing problem of the conservation and restoration of paintings, as well as for the recognition of their authenticity and dating. The identification of paints is also indispensable for the control of their purity. Finally, a knowledge of paint composition is important in view of the fact that often there is a difference between the details supplied on the container and the actual chemical composition, not all paint manufacturers provide catalogues of the chemical compositions of their paints.

Different methods have previously been applied for the analysis of synthetic pigments used in artists' paints, *e.g.*, optical and chemical microscopy, infrared spectrometry, reflexion spectrophotometry, etc. Recently, a spectrophotometric method was used for the identification of pigments which were initially separated by dissolving them in suitable solvent systems¹. However, in all these methods, difficulties arise when chemically similar compounds are to be identified; the task is made even more difficult by the fact that samples are not pure, *i.e.*, homogeneous, in the chemical sense. Therefore, it seems that chromatographic methods of analysis which allow a simultaneous separation and identification of these pigments offer an appropriate solution. Such methods may also be regarded as complementary to those mentioned above.

So far several authors have used thin-layer chromatography (TLC) for the analysis of synthetic organic pigments. Most attention was paid to the analysis of azo pigments which are often encountered. Thus, Mc Clure *et al.*² separated pigments of

the following groups. acetoacetylide, 2-naphthol, 2-hydroxy-3-naphtharylide, dye derivatives, diazo pigments, phthalocyanine and perylene, respectively. Gašparič³ carried out the separation of azo pigments belonging to the acetoacetylide, 2-naphthol, pyrazolone, 2-hydroxy-3-naphtharylide groups, as well as lake azo dyes; in addition to TLC, he also applied paper chromatography. Baier⁴ investigated the TLC of azo and diazo pigments, including sparingly soluble azo pigments and polycyclic pigments. The potential of TLC for the separation of chemically similar pigments whose spectra exhibit only slight differences has also been pointed out by Billmeyer and Kumar¹.

All these investigations were carried out with pure pigments; to our knowledge, no attempt has been made to analyze chromatographically pigments present in artists' paints. In this study we have investigated the possibility of application of TLC to the rapid and efficient separation and identification of synthetic organic pigments most often present in artists' oil and acrylic paints.

EXPERIMENTAL

For TLC separations thin-layers of silica gel H (Type 60; E. Merck, Darmstadt, G.F.R.) were used. Chromatographic plates (20 × 20 cm and 13 × 20 cm) were coated with layers of 300 μm thickness; a mixture of 35 g of silica gel and 85 ml of distilled water was used, which was sufficient for coating 5 or 8 plates, respectively. The coated plates were dried in the air overnight. Pure pigment solutions were chromatographed in parallel with solutions of samples taken from paint tubes. These solutions (2.5–3 mg per 3 ml of the solvent), prepared by heating, were applied to the plate by means of a capillary tube. Spots were dried in a stream of warm air. The development was carried out in commercial tanks for 20-cm plates for 1–1.5 h at 20 ± 2°C. Only in the case of systems 17 and 18, the development time was 3.5 h.

Reagent grade solvents were used for dissolving the samples and for preparation of the solvent systems. Multi-component solvent systems were thoroughly shaken in a separatory funnel before use, and where two layers were obtained the upper layer was applied for chromatography (solvent systems 14 and 20).

The removal of the binding medium from acrylics containing phthalocyanine pigments was effected by multiple extractions with acetone; before extraction, the paints were dried in the air for 24 h. For the removal of the binding medium from oil paints, successive extractions were made with the following solvents: petroleum ether, benzene, ether and acetone. The residue after extraction was dried in a drying oven at 110°C. In the case of other paints it was not necessary to remove the medium, since it was found that this does not affect the separation and R_F values obtained.

All the investigated pigments are in use in the firm Talens (The Netherlands), as were the oil and acrylic paints which belonged to the Rembrandt series.

RESULTS AND DISCUSSION

A list of the pigments investigated is presented in Table I.

Investigations of the solubility of these pigments in a large number of organic solvents have shown that some dissolve in almost all the solvents applied (methanol, cyclohexane, chloroform, acetone), whereas others are either sparingly soluble or

TABLE I
LIST OF INVESTIGATED PIGMENTS

<i>Generic name</i>	<i>Constitution number</i>	<i>Pigment type</i>
Pigment Yellow 1 (PY 1)	11680	Acetoacetarylide
Pigment Yellow 3 (PY 3)	11710	Acetoacetarylide
Pigment Yellow 97 (PY 97)	11767	Acetoacetarylide
Pigment Yellow 100 (PY 100)	19140 1	Metal azo salt
Pigment Yellow 110 (PY 110)		Azamethine pigment (isoindolinone)
Pigment Orange 1 (PO 1)	11725	Acetoacetarylide
Pigment Orange 5 (PO 5)	12075	2-Naphthol
Pigment Orange 43 (PO 43)	71105	Vat Pigment (perinone)
Pigment Red 7 (PR 7)	12420	2-Hydroxy-3-naphtharylide
Pigment Red 12 (PR 12)	12385	2-Hydroxy-3-naphtharylide
Pigment Red 83 (PR 83)	58000 1	'Vat Pigment' (anthraquinone)
Pigment Red 112 (PR 112)	12370	2-Hydroxy-3-naphtharylide
Pigment Red 122 (PR 122)	73915	Quinacridone
Pigment Brown 25 (PBr 25)	12510	Benzimidazolone
Pigment Violet 19 (PV 19)	46500	Quinacridone
Pigment Violet 23 (PV 23)	51319	Dioxazine
Pigment Green 8 (PG 8)	10006	Miscellaneous metal complex pigments
Pigment Green 7 (PG 7)	74260	Phthalocyanine
Pigment Blue 15 (PB 15)	74160	Phthalocyanine

insoluble in the most of the solvents used; however, the last group was found to dissolve in dimethyl sulphoxide, concentrated sulphuric acid and ethanol-sodium hydroxide (9 1), respectively. Accordingly, the pigments were classified into two groups (a) monoazoacetarylide pigments, monoazo-2-naphthols and monoazo-2-hydroxy-3-naphtharylides, (b) metal azo salts, isoindolinones, perinones, quinacridones, monoazobenzimidazolones, anthraquinones, dioxazines, metal complexes and phthalocyanines. Dimethyl sulphoxide was found to be suitable for the most of pigments examined, only PV 23, PO 43 and PR 122 were dissolved in sulphuric acid.

For the chromatographic separation of the pigments more than 150 two- and multi-component solvent systems have been examined; those which were found to afford the best results are listed in Table II.

The chromatographic results for the first group of pigments are shown in Table III. As is seen, the best separations were achieved with solvent system 14. However, better separations of red pigments, which exhibited very similar R_F values, were afforded by solvent system 4.

Chromatographic separation of the second group of pigments presented a complex problem on account of their poor solubility, the pigments either remained at the starting points, or gave diffuse or tailing chromatographic zones. On the basis of investigations carried out with more than 100 solvent systems it has been found that those listed in Table IV allow the identification of some pigments in spite of their similar R_F values, since different colour zones are obtained. For example, the separation of PG 8 from PY 100 and PR 83 can be effected by the use of the solvent system 16, whereas pigments PV 19 and PG 8 which exhibit only slightly different R_F values (only 0.03 R_F units) can be identified on the basis of differently coloured parts of

TABLE II

SOLVENT SYSTEMS USED FOR THE SEPARATION OF PIGMENTS BY TLC ON SILICA GEL H

No.	Composition	Proportion (v/v/v)
1	Pyridine-xylene-acetone	60 40:20
2	Chloroform-toluene-benzene	40 40:40
3	Toluene-pyridine-ethyl acetate	70:30 30
4	Benzene-chloroform-cyclohexane	25:50 25
5	Ethyl acetate-pyridine-toluene-water	30 30 60 10
6	Benzene-cyclohexane-pyridine-water	50:20:20 10
7	Benzene-cyclohexane-pyridine	50 30:20
8	Toluene-acetic acid	70 30
9	Pyridine-toluene	50 50
10	Ethyl acetate-pyridine-acetone	40 40:40
11	Nitrobenzene-xylene	50:50
12	Nitrobenzene-toluene-dimethylformamide	40 40 40
13	Benzene-cyclohexane-chloroform-50% acetic acid	50 20 10:20
14	Benzene-cyclohexane-chloroform-50% acetic acid	60:20 10 10
15	Benzene-cyclohexane-chloroform-50% acetic acid	60:20 15 15
16	Dimethylformamide-dimethylsulphoxide-pyridine-benzene	16:24:40 40
17	Ethanolamine-dimethyl sulphoxide-benzene	20 60:20
18	Ethanolamine-dimethyl sulphoxide-benzene	15:30 55
19	Nitrobenzene-dimethyl sulphoxide-pyridine	25:25 50
20	Formic acid-1,2-dichlorobenzene	80:20

TABLE III

 R_F VALUES OBTAINED FOR THE TLC SEPARATION OF THE FIRST GROUP OF PIGMENTS ON SILICA GEL

Pigments are dissolved in pyridine except where otherwise indicated

Pigment	$R_F \times 100$														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
PY 1	78	34	83	36*	62	83	91	83	50	—	—	—	28*	46*	29*
PY 3	81	43	89	46*	75	90	96	88	66	—	—	—	51*	58*	46*
PY 97	74	1	54	20*	51	65	62	60	18	—	—	—	24*	21*	15*
PY 100	0	0	0	0*	0	0	0	0	0	—	—	—	0*	0*	0*
PY 110	0	0	0	0*	0	0	0	0	0	—	—	—	0*	0*	0*
PO 1	87	—	—	33*	—	—	—	73	78	88	—	—	27*	27*	18*
PO 5	76	—	—	34*	—	—	—	76	72	82	—	—	26*	31*	24*
PO 43	0	—	—	0*	—	—	—	0	0	0	—	—	0*	0*	0*
PR 7	—	—	—	44*	—	—	—	—	—	—	70	94	33*	42*	32*
PR 12	—	—	—	31*	—	—	—	—	—	—	49	85	26*	35*	16*
PR 112	—	—	—	39*	—	—	—	—	—	—	55	89	24*	36*	21*
PR 83	—	—	—	0*	—	—	—	—	—	—	0	81	0*	0*	0*
PR 122	—	—	—	0*	—	—	—	—	—	—	0	0	0*	0*	0*

* Dissolved in dimethyl sulphoxide.

TABLE IV

R_F VALUES OBTAINED FOR THE TLC SEPARATION OF THE SECOND GROUP OF PIGMENTS ON SILICA GEL.

Pigments are dissolved in dimethyl sulphoxide unless otherwise indicated

Pigment	$R_F \times 100$				
	16	17	18	19	20
PBr 25	0-100**	79	0-100**	96(tail)	0
PV 19	97	73-99**	96	93	0
PV 23*	88	98	99	81	92
PG 8	94	97	97	86	89
PY 100	84	100	98	85	65-99**
PY 110	0-100**	76	68-93**	0-100**	0
PG 7	0	0	12	0	0
PB 15	0	0	0	0	0
PR 83	98	99	97	98	99
PR 122*	1	1	2	2	7
PO 43*	2	0	7	3	65

* Dissolved in concentrated sulphuric acid

** In the case of diffuse zones the R_F values of both ends of the spots are given

zones which do not overlap Solvent system 17 is the only one which allows separation of PBr 25 from PY 110. As is seen, PG 7 can migrate from the starting point only upon the application of solvent system 18 Finally, the separation of PO 43 and PR 122, as well as of PV 19 from PR 83, can be achieved by use of solvent system 20 The results obtained show that a given pigment can be chromatographed by the application of several different solvent systems, the actual choice depending on the composition of the sample analyzed

On the basis of these results we attempted to apply this method to the separation and identification of pigments present in about 30 oil and acrylic paints The results of the chromatographic separations are shown in Table V It may be concluded that the analysis of these oil and acrylic paints can be performed with the use of the six solvent systems 4, 14, 16, 17, 18 and 20 Good agreements between the R_F values of pure pigment samples and those obtained for samples taken from paint tubes were achieved It follows that the binding medium has no effect on the separations and R_F values obtained, which makes possible analysis of paint samples without prior removal of this medium. However, in the case of paints containing phthalocyanines the medium has to be removed since it was found to interfere with the chromatography. The identification of the pigments was carried out both on the basis of their R_F values and on the colours of the corresponding spots From the results obtained it can be seen that artists' paints often contain mixtures of pigments, since manufacturers mix different pigments in order to attain various colour tones.

We concluded that the chromatographic method described is very suitable for rapid analysis of synthetic organic pigments in artists' oil and acrylic paints Its advantage lies in its accessibility to small laboratories which are not equipped with expensive and complicated apparatus

TABLE V

CHROMATOGRAPHIC RESULTS FOR SYNTHETIC ORGANIC PIGMENTS IN ARTISTS' OIL AND ACRYLIC PAINTS

<i>Sample number</i>	<i>Sample name</i>	<i>Pigment identified</i>	<i>Solvent system</i>
<i>Oil paints</i>			
1	Talens yellow	PY 1	14
2	Talens yellow lemon	PY 3	14
3	Talens yellow deep	PY 1 + PO 43	14, 20
4	Stil de grain jaune	PY 100	16
5	Dutch vermilion ex.	PO 5	14
6	Madder lake light	PR 83	16
7	Madder lake deep	PR 83	16
8	Rose madder	PR 83	16
9	Rose madder lt (altz)	PR 83	16
10	Talens red purple	PR 12 + PR 112	4
11	Talens red deep	PO 5 + PR 112	14, 4
12	Brownish madder	PBr 25 + PR 83	17
13	Rembrandt rose	PV 19	16
14	Rose madder antique	PV 19	16
15	Asphaltum extra	PY 100 + PG 8 + PR 83	16
16	Stil de grain brun	PV 100 + PG 8 + PR 83	16
17	Permanent violet	PV 23	16
18	Rembrandt blue	PB 15	18
19	Cinnabar green light*	PY 3	14
20	Permanent green light*	PY 3	14
21	Sap green	PY 110 + PG 8	17
22	Rembrandt green	PG 7	18
<i>Acrylic paints</i>			
1	Lemon yellow	PY 3	14
2	Talens yellow light	PY 1 + PY 3	14
3	Talens orange	PO 1	14
4	Talens yellow deep	PY 1 + PO 43	14, 20
5	Carmine	PR 12 + PV 19	4 16
6	Permanent red light	PO 5 + PR 112	14, 4
7	Permanent red deep	PR 7	4
8	Talens rose	PV 19	16
9	Permanent violet	PV 23	16
10	Rembrandt blue	PB 15	18
11	Rembrandt green	PG 7	18

* The green colour of the pigment originates from the inorganic pigment

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REFERENCES

- 1 F. W. Billmeyer and R. Kumar, *J. Chem. Educ.*, 58 (1981) 4
- 2 A. Mc Clure, J. Thompson and J. Tannahill, *J. Oil Colour Chem. Assoc.*, 51 (1968) 580
- 3 G. Gašparič, *J. Chromatogr.*, 66 (1972) 179
- 4 E. Baer, *Farbe und Lack*, 80 (1974) 614.