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Trace analysis of phthalocyanine pigments by high-performance liquid chromatography

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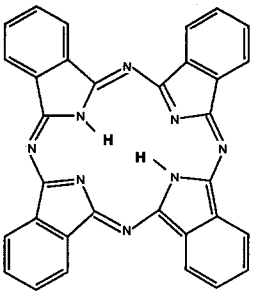
ABSTRACT

A new sensitive and specific method for the analysis of insoluble phthalocyanine pigments is described. In a special microchemical procedure phthalocyanine pigments were converted to the corresponding phthalimides by oxidation, and these were identified by high-performance liquid chromatography and diode-array detection by their retention times and ultraviolet spectra. Detection limits were found to be 2.5 ng for copper phthalocyanine and 27 ng for copper perchlorophthalocyanine. The method was also used for commercial artistic dyes containing copper phthalocyanine.

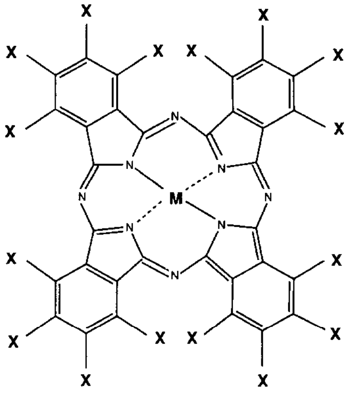
INTRODUCTION

Phthalocyanine (PC), discovered in 1907, has the typical complex ring system (**1**, Fig. 1). The two hydrogen atoms in the center of the molecule can be replaced by various metals. The metal PCs were widely studied and synthesized in the 1920s, commercially introduced for use as pigments in the late 1930s and since that time widely used in dyes and lacquers for artistic and industrial purposes. The most important compounds of this group are phthalocyanine blue (PC blue) (= copper phthalocycanine, CuPC, **2**, Fig. 2)) and phthalocyanine green (PC green) (= copper perchlorophthalocyanine, $CuCl_{16}PC$, **3**, Fig. 2). Both have ideal pigment properties, as they have deep colors, are absolutely insoluble in any solvent except concentrated sulphuric acid and have a very high thermal stability. Sensitive and specific analyses of PCs may be



1 phthalocyanine

Fig. 1. Structure of phthalocyanine (**1**).



2 M = Cu , X = H copper phthalocyanine (CuPC)

3 M = Cu , X = Cl copper perchlorophthalocyanine ($CuCl_{16}PC$)

Fig. 2. Structures of copper phthalocyanine (**2**) and copper perchlorophthalocyanine (**3**).

required in forensic science for the identification of traces of lacquer (*e.g.* of cars) and in archaeometry, where positive PC result in a painting of the twentieth century enables either a dating (introduction of PC-containing artistic dyes = *terminus post quem*) or a decision about authenticity, if the supposed painter had died before the introduction of PCs or if the signature carries an earlier date.

The analytical methods for these important pigments are still mainly restricted to the observation of colors after treatment with concentrated sulphuric or nitric [1] or trichloroacetic acid [2] or N-methylpyrrolidone–alkaline hydrogensulphite solution [3]. There are, however, doubts bout the non-ambiguity of these techniques, especially in dye mixtures [1]. Moreover, the decisions are often very subjective (*e.g.* if the solution should turn "slightly greenish yellow") and the results cannot be easily documented. A combined thin-layer chromatographic (TLC) method which measures the optical reflection spectra directly from the thin-layer plate has been described [4]. Because of their general insolubility, PCs do not migrate during TLC. Therefore no chromatographic result is obtained and a superposition of spectra might often be measured, because quite often several substances remain at the starting position on the TLC plate. There is only one modern method [5], in which the derived phthalic esters are determined by gas chromatography. Unfortunately this three-step reaction cannot be adapted for trace analyses. So the objective of our work was the development of a modern unambiguous trace method, the results of which can be easily documented.

EXPERIMENTAL

Chemicals

CuPC was purchased from Aldrich, $CuCl_{16}PC$ from BASF, potassium dichromate and concentrated sulphuric acid (analytical grade) from Merck and acetonitrile (HPLC grade) from Promochem. The phthalo blue and titan white artistic dyes were manufactured by Schmincke.

Oxidation procedure

The sample was weighed in a special, small, conical glass tube, which was closed at one end (Chrompack Cat. No. 10381, 3 cm long, outer diameter 5 mm reducing to 2 mm). A 20-μl aliquot of concentrated sulfuric acid was added, and the mixture was heated to 80°C for 30 s and put into an ultrasound bath for 2 min. After the addition of 10 μl of a saturated aqueous potassium dichromate solution, the tube was heated to 90°C for 10 min and placed in a brass block with holes of the correct size to hold the tubes and a thermometer. Removal of excess dichromate and dilution of sulphuric acid was carried out by addition of 20 μl of 0.05 *M* sodium hydroxide in methanol–water (1:1, v/v). For commercial dyes, which also contain other materials, centrifugation was carried out while the tube was standing in a septum screw-cap vial (Chrompack Cat. No. 10271); in order to keep it centered in the centrifuge. The supernatant was injected into the HPLC system.

Chromatography

The chromatographic system consisted of an L 6000 Merck–Hitachi pump, a 20-μl sample loop and either an L 4200 Merck–Hitachi UV–VIS detector operating at 219 nm or a Waters 990 diode-array detector. The separation was carried out on a LiChrospher 100 RP-8 (5 μm) column, 120 mm × 4 mm I.D., using acetonitrile–diluted aqueous phosphoric acid at pH 2.8 (20:80) as eluent at a flow-rate of 1.5 ml/min. For the calibration a stock solution of CuPC or $CuCl_{16}PC$ was diluted in concentrated sulphuric acid.

RESULTS AND DISCUSSION

The ideal pigment properties of PC blue and green, insolubility and complete non-volatility, prevent any direct chromatographic analysis, either by HPLC or by gas chromatography. Thus the PC must be converted via a specific reaction to a soluble and easily detectable product. The PC skeleton cleaves to form phthalimide by a well defined oxidation [5,6] (Fig. 3). During this process halogen substituents at the aromatic ring remain unchanged, and $CCl_{16}PC$ yields tetrachlorophthalimide. Dichromate is used as the reagent. The oxidation has been designed for microchemical purposes as a one-vessel procedure. Dissolution of the pigment, reaction at elevated temperature, removal of excess reagent and removal of insoluble sample material were carried out in the same vessel. A special type of small glass tube, conical and closed at one end, was used to keep

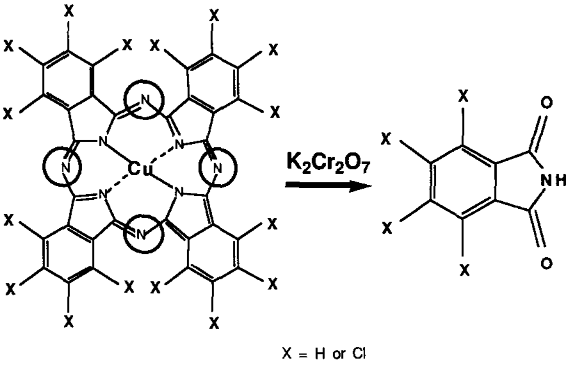


Fig. 3. Oxidation of copper phthalocyanine.

volumes as small as possible and to allow centrifugation of insoluble components of the sample before HPLC analysis. The phthalimides have poor solubilities in organic solvents. However, for an extraction of the unsubstituted PC dichloromethane could be used, and nitrobenzene could be used for the tetrachloro derivative, if the amount of PC was not too large, as indicated by a turbid organic phase. Because mixtures of PC blue and PC green were also possible, no extraction of the oxidation products from the reaction mixture was carried out in the standard procedure. In order to avoid injection of concentrated sulphuric acid, still containing dichromate, onto the column, the dichromate was removed and the acid diluted. This was accomplished by adding 15 μl of a 0.05 *M* solution of sodium hydroxide in methanol–water (1:1, v/v).

The separation and determination of the chlorinated and non-chlorinated phthalimide were performed by isocratic HPLC on an RP-8 phase with optical detection in 7 min (Fig. 4). It should be noted that both compounds adsorb very strongly to any kind of surface, and because of their poor solubility syringes and injection port have to be cleaned very carefully. For this reason a blank check was carried out before each analysis, to rule out contamination from previous samples. Fig. 5 shows the chromatograms of five analyses starting with different amounts of PC blue between 2.5 and 41.8 ng. Only about one third of the resulting reaction mixture was injected into the HPLC system. Even in the presence of the huge amount of sulphuric acid, the phthalimide peak of the smallest sample was still detectable. From the calibration lines based on the weight of the PC sample (Fig. 6) it was shown that the sensitivity for CuCl$_{16}$PC was lower than for the non-chlorinated one. The reasons are, firstly, that in a plot like Fig. 4 the difference in the molecular weights (1120 as compared with 576) is not taken into account, whereas the measured extinction is a molar value. Secondly, the longer retention time (poorer signal-to-noise ratio) and, thirdly, the even higher adsorption contribute to this effect. The first factor results

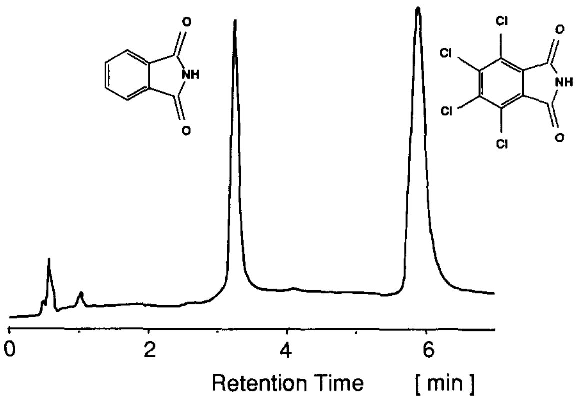


Fig. 4. Separation of phthalimide and tetrachlorophthalimide. Column: LiChrospher RP-8. Mobile phase: acetonitrile–80% diluted aqueous phosphoric acid at pH 2.8 (20:80). Flow-rate: 1.5 ml/min. Detector: photometer operating at 219 nm. For further details see Experimental section.

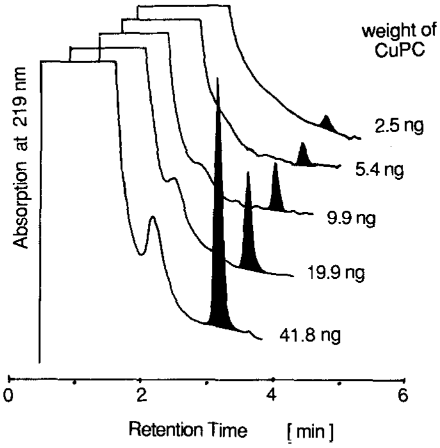


Fig. 5. Chromatograms obtained from the reaction mixtures of copper phthalocyanine and potassium dichromate according to the described procedure (details in the Experimental section). The actual weight of the sample is given to the right of the chromatograms.

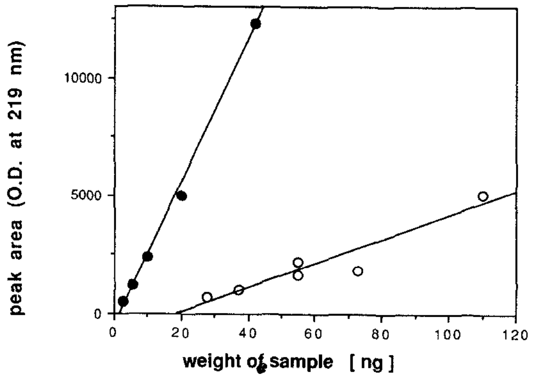


Fig. 6. Calibration at copper phthalocyanine (●) and copper perchlorophthalocyanine (○), determined as the corresponding phthalimide according to the described procedure: phthalimide peak area as a function of the weight of the PC sample.

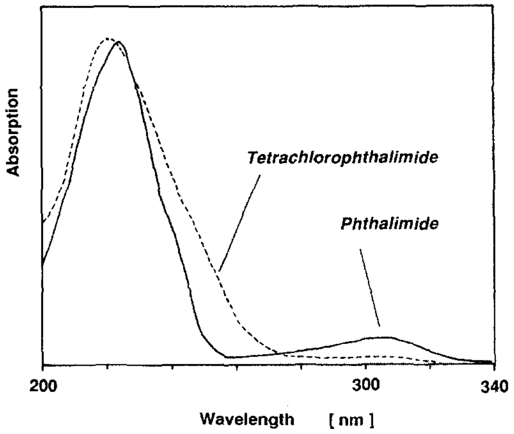


Fig. 7. Optical absorption spectra of phthalimide and tetrachlorophthalimide as measured by a diode-array detector.

in a lower slope of the calibration line, the second leads to a large intercept on the concentration axis and the third factor contributes to both effects.

An even more definite identification of the PCs can be achieved by using a diode-array detector. The spectra of both phthalimides, given in Fig. 7, are quite typical; they have a strong band at about 220 nm and the non-chlorinated a weak supplementary peak at 300 nm. It was found that sufficient chromatographic and spectral results were still obtained from a 0.5-mg sample of dried, light-blue artist dye, prepared from commercial phthalo blue and white dye in a 1:10 weight ratio. The results were not masked by other components, such as binding agents or loading material, which were present in high concentration.

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