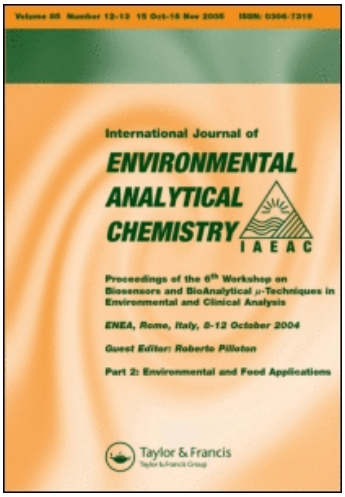

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Analysis of Disperse Yellow 42 in Environmental Samples

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An analytical procedure has been developed for determining low concentrations of Disperse Yellow 42 in natural water and sediment sample. The dye is extracted with organic solvents, cleaned up by adsorption chromatography, concentrated, and analyzed by reversed phase HPLC. A method to identify DY 42 in samples with GC/MS is also described.

KEY WORDS: Dyestuff, analytical determination of disperse dyes, water solubility of DY 42.

INTRODUCTION

Synthetic organic dyes play a significant role in the quality of life.[1] For many commercial dyes risk assessment for possible effects on human health and the environment is available. Whilst toxicological and ecotoxicological properties of modern dyes are being investigated, practically no analytical methods suitable for environmentally significant levels are available.[2] In 1980 the world production and processing losses of dyes and organic pigments were estimated as shown in Table 1.

Although disperse dyes constitute a negligible portion of the total volume of waste in the environment, the availability of methods for

Table 1 World production and losses of dyes[5]

Dye/pigment	*Product* [*t*]	*% losses in*		*Total loss* [*t*]
		Production	*Processing*	
Textile	360 000	2%	10%	43 000
Paper/leader	90 000	2%	5%	7 000
Organic pigment	150 000	1%	1–2%	4 000
Other	40 000	2%	10%	5 000

the determination of small amounts of these dyes is considered important:

—There are no data available on the biodegradation of disperse dyes in natural environments.

—The possible long term health effect makes the availability of a method of determination of these compounds in environmental samples desirable.[3]

—The distribution of disperse dyes in the environment can be observed only with exact knowledge of the concentration of the compound in the different compartments of the environment.

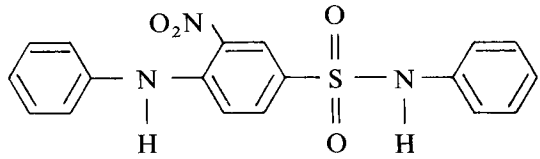
Due to their low solubility in water the disperse dyes must be applied in dispersed form. They are primarily used for dyeing polyester fibres.[4]

After organic pigments (23%) and direct dyes (16%), disperse dyes occupy third place with about 12% of the world production (75 000 t). Disperse dyes are used not only to dye polyester fibres, but also acetate fibres and plastics.[1] To ensure safe handling and use of dyes adequate physicochemical, toxicological and ecological data must be available.

PHYSICOCHEMICAL, TOXICOLOGICAL AND ECOLOGICAL DATA

Physicochemical data of Disperse Yellow 42[6]

chemical structure



formula	$C_{18}H_{15}N_3O_4S$
chemical name	Benzenesulfanilide, 3-nitro-4-phenylamino
colour index name	C.I. Disperse Yellow 42, C.I. No. 10338
molecular weight	369.4
mp	154.5–158.1 °C
bp	n.d.
water solubility	50 ppb[6]
	197 ± 56 ppb (this paper)
log P_{ow}	4.31 ± 0.17 (this paper)
	3.41 RP HPLC (this paper)
	3.02 CLOGP (this paper)
λ_{max}	225 nm, 254 nm, 276 nm, 410 nm

Toxicological data[6]

acute toxicity	LD_{50} p.o.rat > 5000 mg/kg
biological elimination	< 10%
noxious effect against fish	LC_{50} > 1000 mg/l (48 h test)
(orfe)	LC_{50} > 1000 mg/l (48 h test)
noxious effect against	no effect at 1000 mg/l
waste water bacteria	(*pseudomonas fluorescens*)

Ecological data

Disperse Yellow 42 is classified as not readily biodegradable by ETAD.[1] Extensive analysis of the fate of disperse dyes in the environment are not available.

The objective of this study was to develop an analytical procedure for DY 42 concentrations in water and sediment at parts per billion levels, to observe the distribution of DY 42 in water/sediment systems and to follow its degradation in the environment. All this information is necessary for risk assessment.

Background

Commercial dye products normally contain additives such as dispersing agents and reaction products, e.g. salt, sugar and sodium sulfate. To analyse DY 42 in environmental samples it is necessary to prepare pure dye for the use as analytical standard. Such a commercial sample was provided by ETAD (Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry, Basle, Switzerland).

Because of low water solubility the isolation and concentration of the dyestuff from water and sediment was performed by extraction with an organic solvent. DY 42 is very soluble in methanol, dichloromethane, acetonitrile and toluene.

Detection of sediment samples without clean-up appears not to be practicable because many other substances in environmental samples, e.g., chlorophyll and humic substances interfere with the analytical measurement.

The structure and polarity of DY 42 suggested that adsorption liquid chromatography would be the best technique for separation.

There are many possibilities to detect DY 42 in samples.

—chromatographic determination for qualitative analysis (DC, PC)[9]

—photometric determination (visible region) for quantitative analysis (spectral photometer, HPLC-UV)[10]

—mass-spectrometric determination for identification (LC/MS, GC/MS)[11]

The very strong absorption energy in the visible region of the spectrum is the most distinctive characteristic of dyes. This property was selected for development of a method for the quantification of the separated and concentrated dye.

To identify the DY 42 in complex environmental samples the method of GC/MS appears useful, however, quantification and identification of this relative polar compound and metabolites or chemical degradation products seems to be possible by the use of LC-MS.

Determination of the water solubility of DY 42

The OECD-guidelines for testing of chemicals (No. 105)[12] recom-

mend the column elution method to determine the water solubility for material with solubilities below approximately 0.01 g/l. We also used the flask method to confirm the water solubility of DY 42.

EXPERIMENTAL

Analytical parameters

1. HPLC

apparatus	Beckmann
column	ODS-2 (RP-18) Bischof 25 cm, i.d. 4.6 mm particle size 5 μ
eluent	acetonitrile/water 3:1
flow	0.8 ml/min
detection wavelength	410 nm
detection limit	5 ng (100 μl volume)
registration limit	0.1 ppb (100 μl volume)

2. GC/MS

a) mass spectrometer:	HP-MSD 5970 direct coupling
data system:	HP 59970 A
electron energy:	70 eV
ion source temp.:	200 °C
direct coupling temp.:	300 °C
b) gas chromatograph:	HP 5890
temp. program	initial temp: 100 °C 1 min isotherm rate I: 5 °C/min final temp: 320 °C 5 min isotherm
injector temp.:	300 °C splittless
carrier gas:	helium
column:	fused silica cross linked (12 m)
detection limit:	1 ng/μl

Working procedure

Water samples: DY 42 was extracted from 50 or 100 ml samples of water with an equal volume of dichloromethane. The organic phase was dried over anhydrous sodium sulfate, the extract was evaporated

cautiously under pure nitrogen to dryness, dissolved in 1 ml acetonitrile/water 3:1 and analyzed by HPLC.

Sediment samples: Frozen samples from sediment (2–3 g) were shaken with methanol (3 × 50 ml), dried over anydrous sodium sulfate, evaporated at maximally 40 °C under vacuum and concentrated to about 1 ml. The methanol extract was purified by column chromatography on florisil. The dichloromethane fraction was evaporated under nitrogen to dryness and dissolved in acetonitrile/water 3:1. Insoluble components were removed via ultrafiltration (0.45 μm Satorius). The pure extract was analyzed with HPLC. The quantification was carried out with an external standard.

Determination of water solubility of DY 42: As described in the OECD-guidelines, two different masses were added to the top of the preparative HPLC column filled with sea sand as inert material. Water was circulated with a peristaltic pump until saturation of DY 42 (Method 1).[13] For the flask method different portions of pulverised dyestuff were dissolved in water at 60 °C for 24 hr, cooled and kept at room temperature for 48 hr. Undissolved particles were removed by centrifugation until no change in DY 42 concentration was observed (Method 2). The results are given in Table 2.

RESULTS AND DISCUSSION

The absorbance of DY 42 in acetonitrile/water is shown in Figure 1.

The commercial product of DY 42 (Resolin Gelb Bayer) contains 36% dye (as analyzed by HPLC) (Figure 2).

Mass spectrometric analytical identification

The mass spectrum of DY 42 is shown in Figure 3.

In the very sensitive MID (multiple ion detection) mode low levels can be detected. The described measurement can only be used as a method of identification. Because of the evaporation and decomposition of the substance with a gas chromatograph a quantitative determination is not possible.

Table 2 Results of determination of water solubility of DY 42

	Initial mass of DY 42	*Resulting concentration of DY 42 in water*
Method 1	25 mg (90.5 h)	0.137 mg/l
	200 mg (124 h)	0.267 mg/l
Method 2	1.5 mg	0.213 mg/l
	5.0 mg	0.170 mg/l
		0.197 ± 56 mg/l

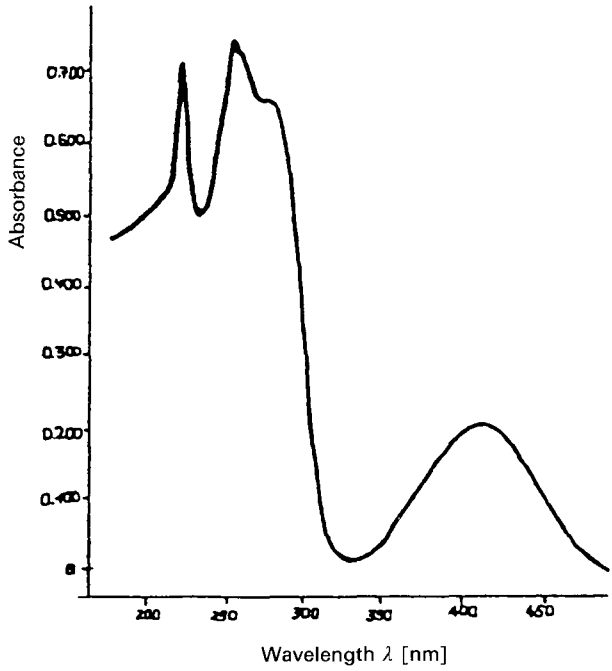


Figure 1 Absorbance of DY 42 in acetonitrile/water 3:1.

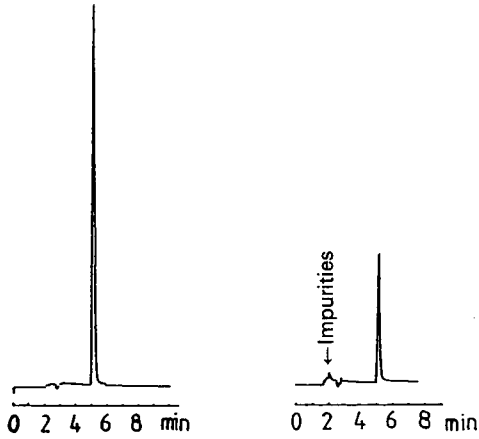


Figure 2 Chromatogram of DY 42 and Resolin Gelb.

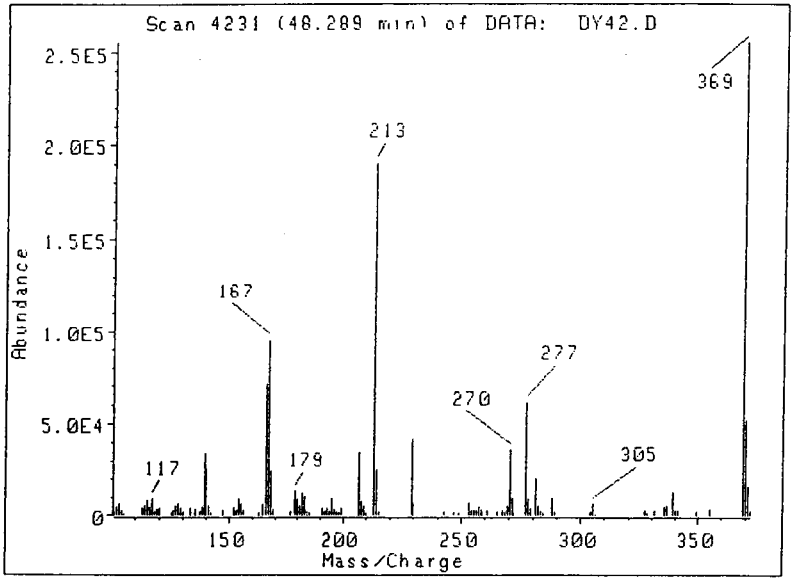


Figure 3 Mass spectrum of DY 42.

Extraction from water

The described method is practical for water samples up to only 30 mg/l dissolved organic matter. To check the extraction efficiency of the described method, water was fortified with known amounts of DY 42, extracted and analyzed by HPLC. Results are given in Table 3.

Extraction of sediment

A number of different extraction procedures have been used. The technique of shaking wet sediment samples with methanol appears to be suitable for the extraction of DY 42 in neutral and slightly alkaline medium. Strong acid and basic media may lead to loss of the substance through cleavage of the sulfanilide group or other changes in the molecular structure. The extraction efficiency of the described method is shown in Table 3.

Table 3 Extraction efficiency of DY 42 and standard deviation

Small type	*Fortification level*	*Average yield/ deviation*
Water/dichloromethane	112 ppb	98.1 ± 2.5 [%]
	11.2 ppb	87.3 ± 2.3 [%]
Water/ethyl acetate	11.2 ppb	84.4 [%]
Sediment neutral/MeOH	10.6 ppm	94.5 [%]
	5.3 ppm	94.9 [%]
Sediment alk./MeOH	21.2 ppm	87.9 [%]
Sediment acid/MeOH	21.2 ppm	60.0 [%]
Sediment/ethyl acetate	21.2 ppm	87.0 [%]

The described analytical procedure makes it possible to analyze a large number of environmental samples. To obtain a reproducible recovery of DY 42 from sediment samples a clean-up is necessary.

Water solubility

The experimental values for water solubility of DY 42 from this study do not agree well with the values from the ETAD study where a solubility of 50 μg/l is reported. The higher value is supported by

the fact that solutions of 100–150 μg/l DY 42 can easily be prepared. The log P_{ow} value estimated as 4.3 in our study however, is in good agreement with the experimental value reported by ETAD (Table 2). The value of log P_{ow} determinated with RP HPLC method and the calculated log P_{ow} from CLOGP program are much too low in comparison to our calculated value of log P_{ow}. CLOGP calculates from the structure of the compound. The program assigns the nitro-group in DY 42 a water solubility much too high when compared with the measured solubility.

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