Table I. Operation Characteristics

(Wall thickness of heat exchanger tubes, $^{5}/_{128}$ inch)

Hg Pressure	Liquor Temp.	Steam Temp.	T	H_2O Evaporated	Glass Surface	H_2O Evaporated	B.t.u./Sq. Ft./Hour/° F.
Mm.	*° F.*	*° F.*		*Lb./hr.*	*Sq. ft.*	*Lb./hr./sq. ft.*	
103	126	212	86	11.40	0.955	11.95	142
85	119	212	93	12.15	0.955	12.73	140
65	109.5	212	102.5	13.15	0.955	13.78	138.5
Operation of 12-liter flask on a steam cone							
97	123.8	212	88.2	10.35	1.88	5.5	66.2

ing merely requires the vacuum to be released, after which the charge will flow out under gravity. To recover the liquor or crystals adhering to the interior walls, it is only necessary to draw up about 50 to 100 cc. of water into the evaporator, allow the vacuum to build to a few hundred millimeters' pressure, and then suddenly open the inlet line. The rapid surge of air up through the heat exchanger tubes throws the small amount of wash liquor around violently, and on releasing the vacuum, it drains out and carries with it the portion of the original charge remaining on the walls of the apparatus.

With pure water this evaporator has the operation characteristics shown in Table I.

The authors have several such units in use in their laboratories, ranging from several times the size shown to small units suitable for handling as little as 100 cc. For the smaller units the heat exchanger is usually made up with only one glass tube through the steam jacket. The jacket is commonly made from scrap thin-walled boiler tubes, with rubber stoppers replacing the two packing glands on the jacket.

This type of evaporator may be fabricated from standard Pyrex tubes and flasks, or may be purchased complete from suppliers of special glass apparatus. (Ace Glass, Inc., has indicated a willingness to fabricate such an apparatus in any size desired.)

Identification of Some Important Unsulfonated Azo-2-naphthol Dyes

LOUIS KOCH, ROBERT F. MILLIGAN, AND SAMUEL ZUCKERMAN
H. Kohnstamm Research Laboratories, Brooklyn, N. Y.

A rapid and simple method has been developed for the identification of unsulfonated azo-2-naphthol dyes, by catalytic reduction of the azo bond, and the separation of the scission products with immiscible solvents, under controlled acid and alkaline conditions. Direct formation of the stable benzoyl derivatives of the reduction products precludes the necessity of isolating sensitive diamines and triamines.

AZO dyes prepared from diazotized primary aromatic amines and 2-naphthol constitute an important series of commercial colors, and their identification is important to the dyestuff chemist. Several analytical methods have been proposed, among which are hydrogenation of the azo bond (*2, 3, 10, 11, 12*), scission of the azo link with fuming nitric acid (*7, 8, 9*), and schematic identification by means of immiscible solvents (*4, 5, 6*).

Whitmore and Revukas (*10, 11*) have shown the applicability of catalytic reduction to azo colors by the use of Raney nickel. Their procedure, however, involves moderately expensive equipment and consumes considerable time when nitrated dyes are hydrogenated, and they report that the isolation and identification of the reduction products are "laborious".

This paper proposes a rapid and simple method for the separation and characterization of the hydrogenation compounds which is based upon their differential solubility in water and ether under varying acid and alkaline conditions.

Cheronis and Koeck (*1*) have devised a simple semimicro hydrogenation apparatus, obtainable from the Wilkens-Anderson Company of Chicago, which the authors find very adaptable to the reduction of azo colors. Utilizing this outfit, it is possible to hydrogenate this series of dyes in peroxide-free dioxane (*11*), smoothly and quickly. Subsequent isolation of the reduction products, by the immiscible solvent procedure, and direct conversion into their benzoyl derivatives, eliminate the necessity of recovering the sensitive free amines.

Partial dehalogenation of chlorinated dyes, an inevitable accompaniment of all attempted reductions in neutral solvents, was overcome by acidification of the peroxide-free dioxane before hydrogenolysis of the color.

GENERAL PROCEDURE

PURIFICATION OF SAMPLES. The coloring matter is purified by crystallization from dioxane, and if or when necessary, water is added to this solvent to induce precipitation.

PREPARATION OF REDUCTION PRODUCTS. Freshly ground Adams-Voorhees platinum oxide (0.05 gram) is placed in the Cheronis hydrogenating unit, and the catalyst is suspended in 25 ml. of peroxide-free dioxane. Hydrogen gas, preferably from a tank, is bubbled through the suspension for 2 to 5 minutes, in order to convert the platinum oxide to colloidal platinum black.

Then 1 gram of dye and 2.5 ml. of concentrated hydrochloric acid are added to the platinum black suspension, the hydrogenating unit is heated by immersion in hot water, 80° to 90° C., and hydrogen gas is passed through the mixture at such a rate that continuous agitation is maintained. (Occasionally, the reduction products will clog the disperser, and it is convenient to have a clean one available for quick replacement. If a second unit is not on hand, it is necessary to remove the clogged disperser, and to clean it by immersion in a test tube containing hot dioxane. At or near the completion of the hydrogenolysis, it is advisable to wash down any dye particles adhering to the sides of the tube, with 5 to 10 ml. of dioxane.)

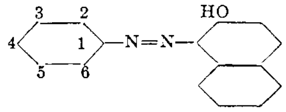
SEPARATION OF THE REDUCTION PRODUCTS. If a precipitate of the reduction products forms in the acidified dioxane solution, it is redissolved by the addition of 5 to 10 ml. of water and filtered into a 500-ml. Squibb separatory funnel. The filtrate is buffered with 250 ml. of a 5% sodium acetate solution, and the ether-soluble amino-2-naphthol, whose presence is indicated by a blue fluorescence, and any primary monoamine, are extracted with two successive 100-ml. portions of ether.

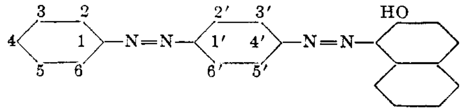
The aqueous layer, containing any water-soluble primary polyamine, is separated from the ether and intimately mixed with 5 ml. of benzoyl chloride. The combined ether fractions are washed with two 50-ml. volumes of water, to remove residual polyamine, and the washings are run into the benzoylation mixture. Then 10 grams of solid sodium hydroxide are added, sufficient to make the aqueous solution alkaline, and after standing at room temperature for 30 minutes, with frequent stirring, the mixture is placed on the steam bath to expel dissolved ether. The benzoyl derivative of the diamine or triamine, which separates as a solid, is filtered off, washed thoroughly with water, and crystallized from a suitable solvent.

Table I. Identification of Unsulfonated Azo-2-Naphthol Dyes

	Dye	Melting Point Observed (uncorrected) ° C.	Melting Point Literature ° C.	Reduction Products of Diazo Component	Melting Point of Benzoyl Derivative of Reduction Product of Diazo Component Observed (uncorrected) ° C.	Melting Point of Benzoyl Derivative of Reduction Product of Diazo Component Literature ° C.	Reduction Time Min.
1.	Benzeneazo-2-naphthol[a, b]	131–2	131	Aniline	162–3[c]	163	15
2.	2-Methylbenzeneazo-2-naphthol	132–3	128	*o*-Toluidine	144–5[c]	145–6	20
3.	4-Ethoxybenzeneazo-2-naphthol	133–4	140	*p*-Phenetedine	172–3[c]	173	25
4.	4-Methylbenzeneazo-2-naphthol	133–4	130	*p*-Toluidine	157–8[c]	157	10
5.	4-Methoxybenzeneazo-2-naphthol	140–1	139	*p*-Anisidine	155–6[c]	156	30
6.	3-Methylbenzeneazo-2-naphthol	140–1	140	*m*-Toluidine	123–4[c]	125	15
7.	2-Ethoxybenzeneazo-2-naphthol	142–3	145	*o*-Phenetedine	Oil	. . .	20
8.	2,5-Dimethylbenzeneazo-2-naphthol	152–3	156	*p*-Xylidine	147–8[c]	140	15
9.	2,4,5-Trimethylbenzeneazo-2-naphthol	155–7	. . .	Pseudocumidine	169–70[c]	162	15
10.	2,4-Dimethylbenzeneazo-2-naphthol[d]	160–1	166	*m*-Xylidine	193–4[c]	192	15
11.	3-Chlorobenzeneazo-2-naphthol	160–1	. . .	*m*-Chloroaniline	120–21[c]	118–20	30
12.	4-Chlorobenzeneazo-2-naphthol[c]	161–2	160	*p*-Chloroaniline	191–2[c]	192–3	30
13.	2-Chlorobenzeneazo-2-naphthol	167–8	167	*o*-Chloroaniline	104–5[e]	99–101	30
14.	2-Methyl-4-chlorobenzeneazo-2-naphthol	170–1	172	2-Methyl-4-chloroaniline	142–3[c, e]	. . .	90
15.	2-Methyl-5-chlorobenzeneazo-2-naphthol	176–7	. . .	2-Methyl-5-chloroaniline	171–2[c, f]	. . .	30
16.	3-Methylbenzeneazo-3′-methylbenzeneazo-2-naphthol	175–7	. . .	*m*-Toluidine 2-Methyl-*p*-phenylenediamine	123–4[c] 301–2[g, h]	125 . . .	20
17.	2-Methoxybenzeneazo-2-naphthol	180–1	180	*o*-Anisidine	Oil	59.8	10
18.	2-Naphthaleneazo-2-naphthol	181–2	174	2-Naphthylamine	160–1[i]	161	20
19.	2,5-Dichlorobenzeneazo-2-naphthol[j]	183–4	. . .	2,5-Dichloroaniline	119–20[c]	120	30
20.	2-Methylbenzeneazo-2′-methylbenzeneazo-2-naphthol	188–9	. . .	*o*-Toluidine 2-Methyl-*p*-phenylenediamine	144–5[c] 301–2[g, h]	145–6 . . .	30
21.	3-Nitrobenzeneazo-2-naphthol	196–7	194	*m*-Phenylenediamine	241–2[g]	240	40
22.	Benzeneazobenzeneazo-2-naphthol	199–200	202	Aniline *p*-Phenylenediamine	162–3[c] 338–9[g]	163 Over 300	90
23.	2-Nitro-4-methoxybenzeneazo-2-naphthol	206–7	. . .	4-Methoxy-*o*-phenylenediamine	251–2[g]	251–2	65
24.	5-Nitro-2-methylbenzeneazo-2-naphthol	210–11	206	1-Methyl-2,4-phenylenediamine	225–6[g]	224	45
25.	2-Nitrobenzeneazo-2-naphthol	213–4	212	*o*-Phenylenediamine	303–4[g]	301	30
26.	1-Naphthaleneazo-2-naphthol	232–3	224	1-Naphthylamine	158–9[i]	156, 161–2	20
27.	4-Nitro-2-methylbenzeneazo-2-naphthol	251–2	248	2-Methyl-1,4-phenylenediamine	301–2[g, h]	. . .	30
28.	4-Chloro-2-nitrobenzeneazo-2-naphthol[k]	255–6	252	4-Chloro-*o*-phenylenediamine	226–7[d]	230	55
29.	2,5-Dimethylbenzeneazo-2′,5′-dimethylbenzeneazo-2-naphthol	263–4	. . .	*p*-Xylidine 2,5-Dimethyl-*p*-phenylenediamine	147–8[c] 311–12[g, l]	148 . . .	120
30.	2-Nitro-4-methylbenzeneazo-2-naphthol	273–4	278	4-Methyl-*o*-phenylenediamine	263–4[g]	263–4	150
31.	2-Chloro-4-nitrobenzeneazo-2-naphthol[m]	289–90	282	2-Chloro-*p*-phenylenediamine	239–40[c]	228	50
32.	2,4-Dinitrobenzeneazo-2-naphthol[n]	312–13	302	1,2,4-Triaminobenzene	278–9[o, p]	260	50

[a] The nomenclature follows the numbering systems shown below:





[b] The benzoyl derivative of amino-2-naphthol, from all compounds investigated, was recrystallized from ethanol, M.P. observed 232–3° C. (uncorrected); M.P. literature, 226.5°, 235.5° C.

[c] Solvent, ethanol-water.

[d] To differentiate further between compounds 10 and 12, analyze for presence of halogen by any accepted procedure.

[e] Monobenzoyl derivative, $C_6H_3.CH_3.Cl.NHCOC_6H_5$. Chlorine calculated, 14.44%; found, 14.40%.

[f] Monobenzoyl derivative, $C_6H_3.CH_3.Cl.NHCOC_6H_5$. Chlorine calculated, 14.44%; found 14.47%.

[g] Solvent, acetic acid.

[h] Dibenzoyl derivative, $C_6H_3.CH_3.(NHCOC_6H_5)_2$. Nitrogen calculated 8.48%; found, 8.50%.

[i] Solvent, ethanol.

[j] 2,5-Dichloroaniline did not wash out of ether layer with *N* hydrochloric acid. It was isolated by evaporating ether and crystallizing residue from ethanol-water; M.P. 49° C. (uncorrected).

[k] Nearly all the diazo component was found as 4-chloro-2-nitraniline in ether layer, M.P. 117–18° C. (uncorrected). Its benzoyl derivative melted at 131–2° C. (uncorrected).

[l] Dibenzoyl derivative, $C_6H_2(CH_3)_2(NHCOC_6H_5)_2$. Nitrogen calculated, 8.14%; found, 8.18%.

[m] About one half of, diazo component was found in ether layer as 2-chloro-4-nitraniline, M.P. 107–8° C. (uncorrected). Its benzoyl derivative melted at 157–8° C. (uncorrected).

[n] About one half of diazo component was found unreduced to triamine form and was isolated from ether layer as 2,4-dinitraniline, M.P. 178–9° C. (uncorrected).

[o] Solvent, acetic acid–water.

[p] Benzoyl derivative of triamine (1,2,4-triaminobenzene) isolated from reduction of *p*-ethoxybenzeneazo-*m*-phenylenediamine, had same M.P.

Amphoteric amino-2-naphthol is separated from the primary monoamine, by removing the former with four successive 50-ml. portions of 2% sodium hydroxide solution, followed by two 50-ml. volumes of water, and is isolated as the benzoyl derivative by running the alkaline extracts into 5 ml. of benzoyl chloride, stirring vigorously after each addition. Dissolved ether is eliminated by heating on the steam bath, and after cooling to room temperature, the benzoyl derivative is filtered off, washed thoroughly with water, and crystallized from ethanol.

The ether solution, containing the primary monoamine, is shaken with four 50-ml. portions of *N* hydrochloric acid, followed by a 50-ml. volume of water. Dissolved ether is expelled by heating, and the acid solution is cooled. Ten grams of solid sodium hydroxide are added to liberate the free amine, and the mixture is treated with 5 ml. of benzoyl chloride. Upon vigorous agitation, the benzoyl derivative separates as a pasty mass, which is allowed to stand overnight. It is then filtered off, washed thoroughly with water, and crystallized from a suitable solvent.

If the melting point of the purified dye indicates the presence of 2,5-dichlorobenzeneazo-2-naphthol, 2,4-dinitrobenzeneazo-2-naphthol, 2-chloro-4-nitrobenzeneazo-2-naphthol, or 4-chloro-2-nitrobenzeneazo-2-naphthol, the residual ether is evaporated on a steam bath, and the residue is identified according to the directions given in the footnotes to Table I.

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