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## Determination of aromatic amines formed from azo colorants in toy products

M.C. Garrigós<sup>a</sup>, F. Reche<sup>a</sup>, M.L. Marín<sup>b</sup>, A. Jiménez<sup>a,\*</sup>

<sup>a</sup>Department of Analytical Chemistry, University of Alicante, PO Box 99, 03080 Alicante, Spain

<sup>b</sup>Institute of Toy Technology (AIJU), Av. Industria 23, 03440, Ibi, Alicante, Spain

### Abstract

A study for the determination of the aromatic amines formed after reduction of the azo colorants mostly used in toys was conducted. Sodium dithionite was used in the reductive cleavage of the azo group for the dyes, and the released amines were subsequently analysed by high-performance liquid chromatography with UV detection. The influence of different variables related to the reduction process was investigated by the use of a full-level factorial design, where most significant parameters as well as order interactions were studied. Reduction profiles for each colorant were obtained by studying the changes in the amount of amine obtained with different dithionite/colorant ratios. The expected aromatic amines forming azo colorants were detected, and in the presence of a nitro group a further reduction was observed. The yield of the total reduction process was determined by using standard addition of different quantities of amines to the colorants.

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### 1. Introduction

Azo dyestuffs are widely used as colorants in a variety of products such as food, paper, leather, cosmetics, medicines, toys, plastics, printing links, paints, textiles, etc. [1]. They are commonly prepared by coupling a diazotized aromatic amine with a phenol or another aromatic amine [2]. But some studies have stated the potential toxicity of azo dyes, which arises from the reduction of the azo group, by the action of intestinal anaerobic bacteria or the hepatic azo reductases with the release of some aromatic amines [3,4]. These released aromatic

amines can react in cells leading to the initiation of the carcinogenic process [5–8].

Several analytical methods for the determination of aromatic amines in dyes have been described in the literature. These methods were applied to the determination of amines in specific matrices, such as industrial effluents [9–11] and inks [12], but most of them were applied to textiles and leather [13–18]. The general process consisted of the reductive cleavage of dye samples with sodium dithionite in an aqueous media, followed by solvent extraction and further determination of the amines by liquid or gas chromatography.

As a result of the potential toxicity of azo compounds, the European Normalisation Committee (CEN) is willing to set some requirements for coloring agents (including azo) with reference to the safety of toys. Therefore, the development of fast,

\*Corresponding author. Tel.: +34-96-590-3777; fax: +34-96-590-3781.

E-mail address: [alfjimenez@ua.es](mailto:alfjimenez@ua.es) (A. Jiménez).

reproducible and efficient analytical methods for the determination of aromatic amines, to monitor the presence of azo dyes and assess the risk of the toy products is necessary. However, none of the methods previously reported were ever applied to toy products. Therefore, the development of an analytical method for the determination of colorants mostly used in such samples (insoluble in aqueous solvents) with the corresponding aromatic amines has to be considered.

Most analytical processes are influenced by a wide variety of factors, and, when monitoring them, unexplained variations can occur. Moreover, which factors are most significant is not always obvious at first inspection. Experimental design methodology can be considered as an effective tool for the simultaneous study of the influence of several parameters, obtaining more information with as few runs as possible by varying several factors at once [19]. They also permit the detection and estimation of any interaction which classical experiments cannot carry out [20].

The work presented here includes optimisation of

experimental conditions for the determination of aromatic amines formed from the reduction of azo colorants mostly used in toys. The reductive cleavage procedure includes the use of sodium dithionite. The effects of temperature, time and dithionite/colorant (dit/col) ratio on the reductive cleavage process were investigated simultaneously by a 2<sup>3</sup> factorial design. HPLC was used for the separation and quantitative determination of such compounds.

## 2. Experimental

### 2.1. Chemicals and samples

Analytical grade standards of the 24 aromatic amines considered in this work were obtained from Sigma (St. Louis, MO, USA) and are listed in Table 1. Stock solutions of each compound (20 µg/g) were prepared in methanol (LC grade) obtained from Merck (Darmstadt, Germany).

Nine of the most used dyes in the toy industry [21,22], identified by their CI name and CAS number

Table 1  
Aromatic amines considered in this work

| Aromatic amine                         | CAS number | $\lambda_{\max}$ (nm) | Molar mass (g/mol) |
|--|------------|-----------------------|--------------------|
| 4,4'-Methylenbis(2-chloroaniline)      | 101-14-4   | 244                   | 267.16             |
| Aniline                                | 62-53-3    | 231                   | 93.13              |
| 1,4-Diaminobenzene                     | 106-50-3   | 239                   | 108.14             |
| 2-Chloro-1,4-diaminobenzene            | 615-66-7   | 243                   | 142.59             |
| 4-Nitroaniline                         | 100-01-6   | 227                   | 138.13             |
| 2-Amino-4-nitrotoluene                 | 99-55-8    | 246                   | 152.15             |
| <i>o</i> -Aminoazotoluene              | 97-56-3    | 251                   | 225.30             |
| 2,4,5-Trimethylaniline                 | 137-17-7   | 232                   | 135.21             |
| 2,4-Diaminotoluene                     | 95-80-7    | 230                   | 122.17             |
| <i>o</i> -Toluidine                    | 95-53-4    | 230                   | 107.16             |
| 4,4'-Thiodianiline                     | 139-65-1   | 260                   | 216.31             |
| 4,4'-Oxidianiline                      | 101-80-4   | 244                   | 200.24             |
| <i>p</i> -Cresidine                    | 120-71-8   | 232                   | 137.18             |
| 4,4'-Methylene di- <i>o</i> -toluidine | 838-88-0   | 241                   | 226.32             |
| 3,3'-Dimethylbenzidine                 | 119-93-7   | 280                   | 212.30             |
| 3,3'-Dimethoxybenzidine                | 119-90-4   | 300                   | 244.30             |
| Benzidine                              | 92-87-5    | 280                   | 184.10             |
| 2-Naphthylamine                        | 91-59-8    | 233                   | 143.20             |
| 4-Aminobiphenyl                        | 92-67-1    | 275                   | 169.20             |
| 4-Chloro- <i>o</i> -toluidine          | 95-69-2    | 239                   | 141.60             |
| 4-Chloroaniline                        | 106-47-8   | 239                   | 127.57             |
| 4,4'-Methylenedianiline                | 101-77-9   | 241                   | 198.27             |
| 3,3'-Dichlorobenzidine                 | 91-94-1    | 284                   | 253.00             |
| 2,4-Dimethylaniline                    | 95-68-1    | 233                   | 121.18             |

(Table 2), were evaluated in this study. Analytical grade standards of dyes, sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), sodium hydrogenphosphate ( $\text{Na}_2\text{HPO}_4$ ) and sodium dihydrogenphosphate ( $\text{NaH}_2\text{PO}_4$ ) were also obtained from Sigma (St. Louis, MO, USA). The water was distilled and passed through a Milli-Q Water System (Millipore, Bedford, MA, USA) prior to use.

## 2.2. Reduction procedure

Stock solutions of each dye in methanol ( $\sim 7 \mu\text{g/g}$ ) were prepared. Three dyes were selected for the optimisation of reduction: Solvent Yellow 14, Solvent Red 24 (a diazo dye) and Disperse Red 1. A full  $2^3$  factorial design for each dye was carried out in order to optimise the main reduction parameters. First  $\sim 5 \text{ g}$  of the dye solution (equivalent to  $40 \mu\text{g}$  of dye) was weighed into a round bottomed dark flask and placed into a shaking heater until the required temperature was reached. Then,  $20 \mu\text{l}$  of a freshly prepared  $\text{Na}_2\text{S}_2\text{O}_4$  solution with an adequate concentration to achieve the required dit/col ratio (% (w/w) in water), were added to the flask and left for the required time to accomplish the reaction. The flask was then placed in an ice bath until the solution cooled to room temperature and then the extract was immediately analysed by HPLC.

## 2.3. Analysis

Analysis of aromatic amines was carried out by HPLC, using a Waters liquid chromatograph (Milford, MA, USA) equipped with a 600E multisolvent delivery system, an in-line degasser, and a 996 UV-visible photodiode array detector. Chromatographic conditions included a Tracer Excel 120 ODSA column ( $5 \mu\text{m}$ ,  $25 \times 0.46 \text{ cm}$ ; Teknokroma, Barcelona, Spain),  $20 \mu\text{l}$  injection volume and  $1 \text{ ml/min}$  flow-rate. A methanol-phosphate buffer ( $30 \text{ mM}$   $\text{NaH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$ , pH 6.9) gradient (50%, 13-min hold, to 80% methanol in 0.5 min with 16.5-min hold) was used. Quantification of amines was performed by comparing chromatographic peak areas for sample extracts with those of standards in the same concentration range. An example of the HPLC-UV separation of the 24 amines is shown in Fig. 1. All aromatic amines can be adequately

determined at their maximum absorbance wavelength. Only aniline and 4-nitroaniline as well as 4-chloroaniline and 2-amino-4-nitrotoluene peaks, appear at similar retention times. As each amine considered in this work is an eventual degradation product of azo colorants, it is not likely that more than one from an individual azo colorant sample will be found.

## 3. Results and discussion

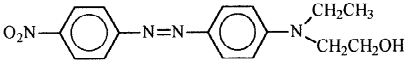
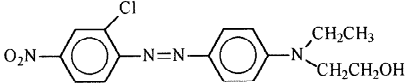
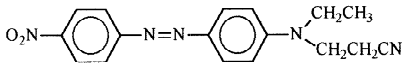
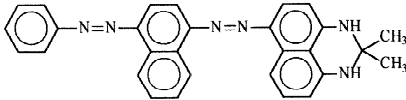
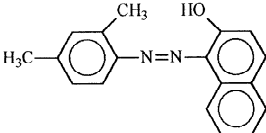
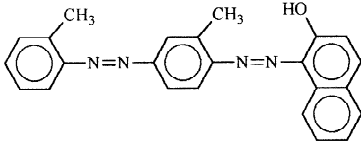
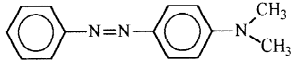
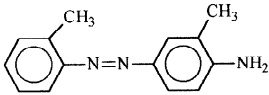
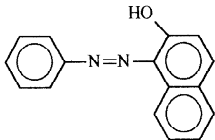
Calibration curves for the 24 aromatic amines selected for this study were run at five concentration levels using appropriately diluted standards. Each concentration level was injected in triplicate, and chromatographic peak areas were fitted by linear regression. The linearity range was  $0.2$ – $20 \mu\text{g/g}$  with a correlation coefficient higher than 0.9999.

### 3.1. Optimisation of reduction

The effect of the main reduction parameters was studied by a three-factor design with two levels for each factor (low and high). This design requires eight experiments plus one in the middle, which were performed in duplicate and were run randomised. Table 3 lists the design matrix for experiments, as well as the values given to each factor. The investigated parameters were temperature ( $T$ ), reaction time ( $t$ ) and dithionite/colorant (dit/col) ratio ( $r$ ), and were optimised to maximise the yield of reduction products detected while minimising the amount of the parent dye remaining. The presence of the dye in the solutions after reduction was checked at the same HPLC amine conditions. In the case of higher molar weight dyes, flow-rate was increased to 100% methanol after the corresponding amines gradient program, to elute dyes in a reasonable time.

Maximum reduction of dyes was observed for experiment 4 ( $65^\circ\text{C}$ , 20 dit/col ratio and 5 min). Total decoloration of the solution was observed in each case at these conditions; therefore, it can be assumed that the azo cleavage was completed. A statistical analysis of results was performed considering all possible interactions as seen in Fig. 2, where only significant effects (95% probability) as well as one second-order interaction are presented. From this

Table 2  
General properties of the dyes evaluated in this work

| Dye                | CAS number  | CI number   | Molar mass (g/mol) |        |
|--------------------|---|-------------|--------------------|--------|
| Disperse Red 1     |    | 2872-52-8   | 11 110             | 314.35 |
| Disperse Red 13    |    | 3180-81-2   | 11 115             | 348.79 |
| Disperse Orange 25 |    | 31 482-56-1 | 11 227             | 323.36 |
| Solvent Black 3    |    | 4197-25-5   | 26 150             | 465.55 |
| Solvent Orange 7   |   | 3118-97-6   | 12 140             | 276.34 |
| Solvent Red 24     |  | 85-83-6     | 26 105             | 380.45 |
| Solvent Yellow 2   |  | 60-11-7     | 11 020             | 225.30 |
| Solvent Yellow 3   |  | 97-56-3     | 11 160             | 225.30 |
| Solvent Yellow 14  |  | 842-07-9    | 12 055             | 248.29 |

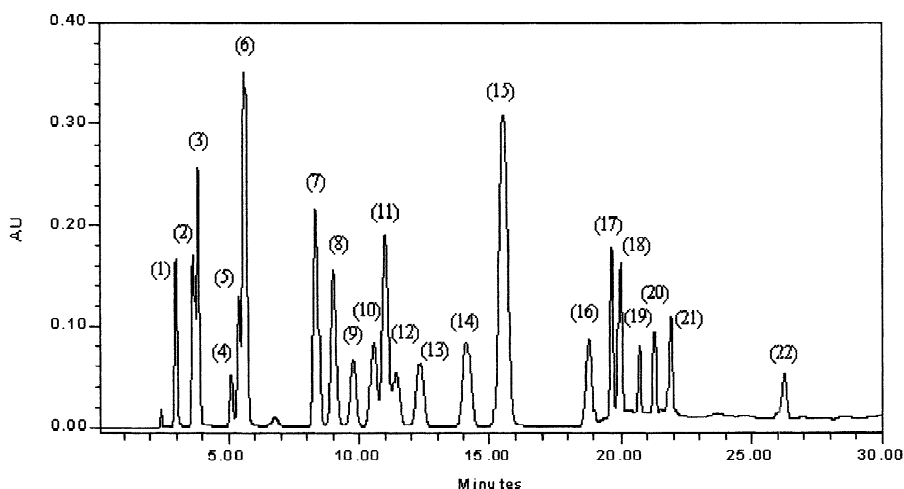


Fig. 1. HPLC–UV chromatogram at 230 nm for the analysis of the aromatic amines listed. (1) 1,4-Diaminobenzene; (2) 2-cloro-1,4-diaminobenzene; (3) 2,4-diaminotoluene; (4) benzidine; (5) 4,4'-oxidianiline; (6) aniline and 4-nitroaniline; (7) *o*-toluidine; (8) 4,4'-methylenedianiline; (9) 3,3'-dimethoxybenzidine; (10) 3,3'-dimethylbenzidine; (11) 4-chloroaniline and 2-amino-4-nitrotoluene; (12) 4,4'-thiodianiline; (13) *p*-cresidine; (14) 2,4-dimethylaniline; (15) 2-naphtylamine; (16) 4-cloro-*o*-toluidine; (17) 4,4'-methylene di-*o*-toluidine; (18) 2,4,5-trimethylaniline; (19) 4-aminobiphenyl; (20) 3,3'-dichlorobenzidine; (21) 4,4'-methylenbis(2-chloroaniline); and (22) *o*-aminoazotoluene.

Table 3

Factor levels and design matrix in the  $2^3$  factorial design for the reduction process

| Factor        | Units    | Levels  | Run      |            |       |   |   |   |   |   |   |   |   |   |
|---------------|----------|---------|----------|------------|-------|---|---|---|---|---|---|---|---|---|
| Variable      | Key      | Low (-) | High (+) | Middle (0) | 1     | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |   |
| Temperature   | <i>T</i> | °C      | 50       | 65         | 57.5  | - | + | - | + | - | + | - | + | 0 |
| Dit/col ratio | <i>r</i> | -       | 2.5      | 20         | 11.25 | - | - | + | + | - | - | + | + | 0 |
| Reaction time | <i>t</i> | min     | 5        | 25         | 15    | - | - | - | - | + | + | + | + | 0 |

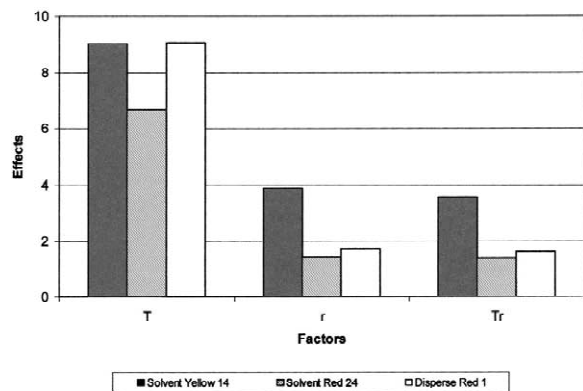


Fig. 2. Standardised significant effects for chemical reduction of dyes.

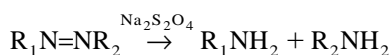
figure, we can conclude that for all dyes, time does not seem to be significant (even for the diazo dye Solvent Red 24), temperature being the most significant variable followed by dit/col ratio. The *Tr* interaction in all cases again reflects the positive importance of these two parameters in the reduction process.

### 3.2. Release of aromatic amines

HPLC analysis of the reduced azo dyes confirmed the presence of aromatic amines generated by splitting the azo linkage (Table 4). These aromatic amines were not detected in the HPLC analysis of dyes prior to reduction. Of the three dyes tested, Solvent Yellow 14 and Solvent Red 24 formed the anticipated aromatic amines after reduction:

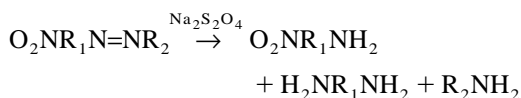
Table 4  
Reduction products of aromatic amines identified from the azo colorants evaluated

| Azo colorant       | Reduction products          |
|--------------------|-----------------------------|
| Disperse Red 1     | 1,4-Diaminobenzene          |
| Disperse Red 13    | 2-Chloro-1,4-diaminobenzene |
| Disperse Orange 25 | 1,4-Diaminobenzene          |
| Solvent Black 3    | Aniline                     |
| Solvent Orange 7   | 2,4-Dimethylaniline         |
| Solvent Red 24     | <i>o</i> -Toluidine         |
| Solvent Yellow 2   | Aniline                     |
| Solvent Yellow 3   | <i>o</i> -Toluidine         |
| Solvent Yellow 14  | Aniline                     |



But, for Disperse Red 1, two different reduction products were found depending on experimental conditions. At experiments at low temperature and dit/col ratio, 4-nitroaniline (the expected amine) was found, but at higher conditions 1,4-diaminobenzene appeared instead. In fact, the presence of a nitro group in the dye usually results in the formation of a diamine [9,10]. In this case, the first aromatic amine (4-nitroaniline) was further reduced to form the

corresponding aromatic amine 1,4-diaminobenzene according to the following:



There were some experiments where the two amines co-appeared, and others where there was only one. Reduction profiles for each colorant were obtained by studying the changes in the amount of amine obtained with dithionite/colorant ratio, at 65 °C and 5 min. Those results are shown in Fig. 3. For Disperse Red 1 the sum of 4-nitroaniline and 1,4-diaminobenzene amounts is displayed, to give an idea of the total reduction yield. As can be seen, in all cases there is a dit/col ratio where the maximum quantity of aromatic amine, along with total decoloration of solution and absence of dye, is obtained. This ratio seems to be ~10 for all dyes. For higher dit/col ratios, the amount of aromatic amine obtained from each dye remains practically constant, except for Disperse Red 1, where a decrease in response is observed. The amount of each aromatic amine obtained in the reduction of Disperse Red 1 for each dit/col ratio is shown in Fig. 4. As can be

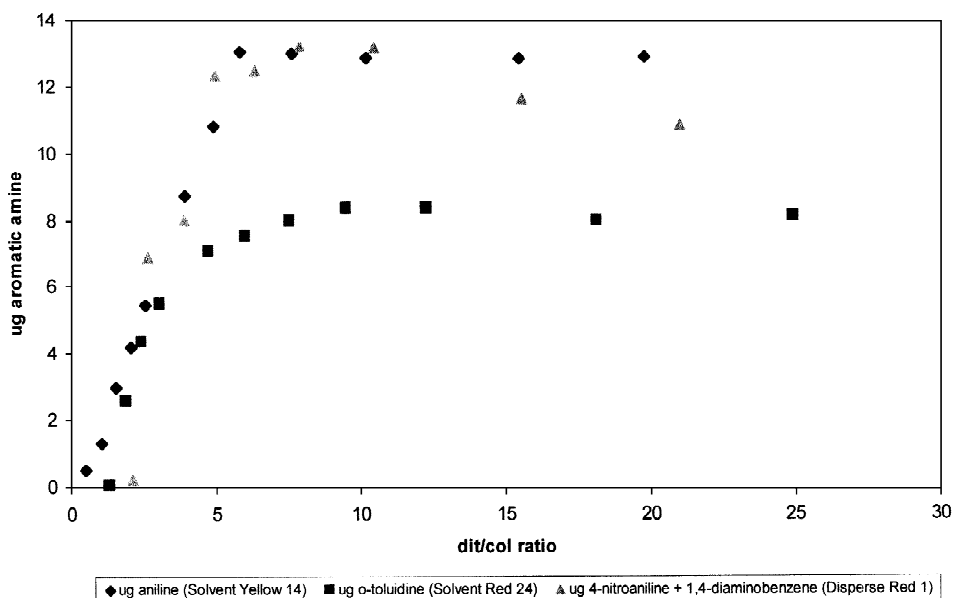


Fig. 3. Reduction profiles for the studied dyes.

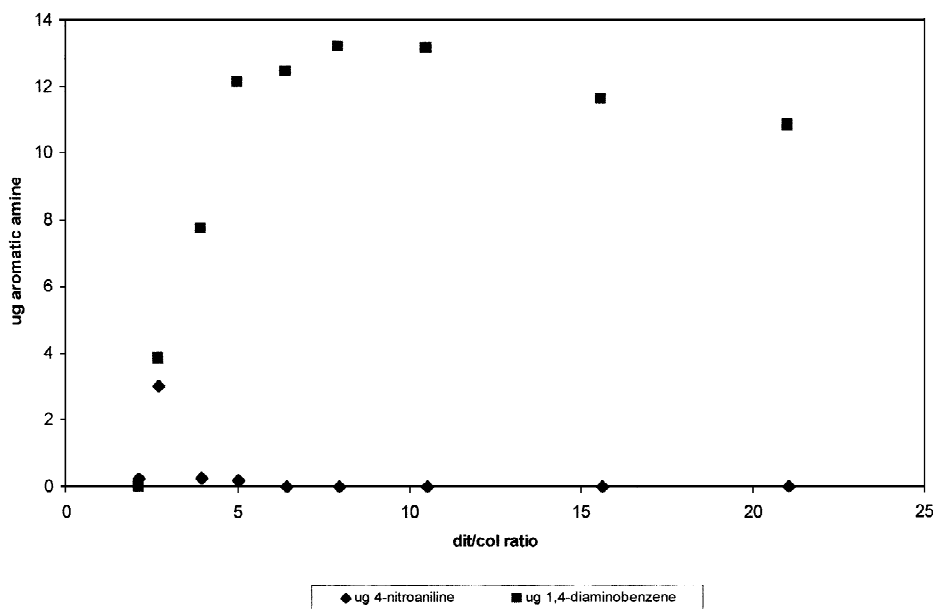


Fig. 4. Reduction profiles for Disperse Red 1 showing the different aromatic amines found.

observed, only 4-nitrotoluene is obtained at the lowest dit/col ratio, with experiments where the two amines co-appear at higher ratios with finally only 1,4-diaminobenzene being found at the highest. Therefore, the decrease in response is only due to the amount of 1,4-diaminobenzene, and we assume that other cleavage products can arise with an excess of dithionite in the reduction solution.

The optimum reduction conditions (65 °C, dit/col ratio 10, and 5 min) were applied to the other colorants, their main reduction products being shown in Table 4. As in the case of Disperse Red 1, Disperse Red 13 and Disperse Orange 25 have also an NO<sub>2</sub> group in the first aromatic amine liberated by the reduction procedure. Therefore, this group was again further reduced obtaining the corresponding aromatic amines shown in Table 4.

### 3.3. Recovery of reduction process

The reduction process was further applied to the free aromatic amines in order to evaluate the influence of the process on the recovery of amines. Of all of them only 21 were considered, since 4-nitroaniline, 2-amino-4-nitrotoluene and *o*-amino-

azotoluene undergo a self-reduction to form 1,4-diaminobenzene, 2,4-diaminotoluene and *o*-toluidine, respectively. In order to cover all the possibilities for reduction, three kinds of experiments were carried out, i.e. the complete reduction process, the reduction at room temperature and the process with no addition of sodium dithionite. Table 5 shows the mean recoveries obtained for the amines studied in each case. Acceptable values are obtained for all the amines, with similar results for the three processes evaluated.

In order to determine the effectiveness and recovery of the total reaction process, standard addition of different quantities of the corresponding aromatic amines to the colorants Solvent Yellow 14, Solvent Red 24 and Disperse Red 1 was carried out, and reduction process was accomplished. Results are shown in Fig. 5. Reduction yield was calculated as the theoretical amount of amine according to the graph, relative to the experimental amount of amine found in the reduction process of the colorant with no addition. This results in 82.2% for aniline in Solvent Yellow 14, 99.8% for *o*-toluidine in Solvent Red 24 and 87.1% for 1,4-diaminobenzene in Disperse Red 1. These values are very similar to those

Table 5  
Mean recoveries (%) of aromatic amines in the reduction process

| Amine                                  | 65 °C, dit/col 10, 5 min |         | dit/col 10, 5 min |         | 65 °C, 5 min      |         |
|--|--------------------------|---------|-------------------|---------|-------------------|---------|
|  | Mean <sup>a</sup>        | RSD (%) | Mean <sup>a</sup> | RSD (%) | Mean <sup>a</sup> | RSD (%) |
| 4,4'-Methylenbis(2-chloroaniline)      | 93.4                     | 1.7     | 93.1              | 1.2     | 96.7              | 0.6     |
| Aniline                                | 89.2                     | 1.2     | 88.0              | 2.2     | 88.5              | 1.7     |
| 1,4-Diaminobenzene                     | 96.0                     | 2.1     | 98.9              | 0.9     | 95.0              | 1.3     |
| 2-Chloro-1,4-diaminobenzene            | 97.1                     | 2.3     | 97.9              | 2.1     | 98.3              | 1.8     |
| 2,4,5-Trimethylaniline                 | 86.4                     | 3.0     | 84.0              | 0.1     | 86.4              | 2.1     |
| 2,4-Diaminotoluene                     | 96.1                     | 2.1     | 97.7              | 2.7     | 99.4              | 2.7     |
| <i>o</i> -Toluidine                    | 99.6                     | 2.3     | 98.9              | 3.0     | 97.6              | 2.1     |
| 4,4'-Thiodianiline                     | 84.8                     | 1.6     | 86.5              | 1.8     | 86.1              | 2.0     |
| 4,4'-Oxidianiline                      | 82.2                     | 0.7     | 84.3              | 1.9     | 87.4              | 1.3     |
| <i>p</i> -Cresidine                    | 97.6                     | 0.6     | 99.1              | 3.2     | 97.3              | 3.1     |
| 4,4'-Methylene di- <i>o</i> -toluidine | 94.1                     | 2.6     | 93.5              | 2.7     | 95.7              | 0.8     |
| 3,3'-Dimethylbenzidine                 | 99.3                     | 1.6     | 99.1              | 2.1     | 99.0              | 1.8     |
| 3,3'-Dimethoxybenzidine                | 97.8                     | 3.4     | 98.3              | 2.9     | 98.6              | 2.5     |
| Benzidine                              | 89.1                     | 2.6     | 90.8              | 3.8     | 93.8              | 1.6     |
| 2-Naphtylamine                         | 97.9                     | 3.3     | 97.6              | 2.5     | 99.3              | 1.5     |
| 4-Aminobiphenyl                        | 93.6                     | 3.1     | 91.1              | 2.8     | 91.9              | 0.7     |
| 4-Chloro- <i>o</i> -toluidine          | 97.9                     | 0.3     | 98.5              | 0.8     | 99.6              | 2.0     |
| 4-Chloroaniline                        | 90.9                     | 1.5     | 90.8              | 0.4     | 92.9              | 0.6     |
| 4,4'-Methylenedianiline                | 92.4                     | 1.8     | 97.3              | 3.0     | 96.2              | 3.0     |
| 3,3'-Dichlorobenzidine                 | 98.8                     | 1.2     | 97.3              | 2.3     | 98.3              | 2.8     |
| 2,4-Dimethylaniline                    | 89.0                     | 1.1     | 88.9              | 0.9     | 92.3              | 2.1     |

<sup>a</sup> Based on three replicates.

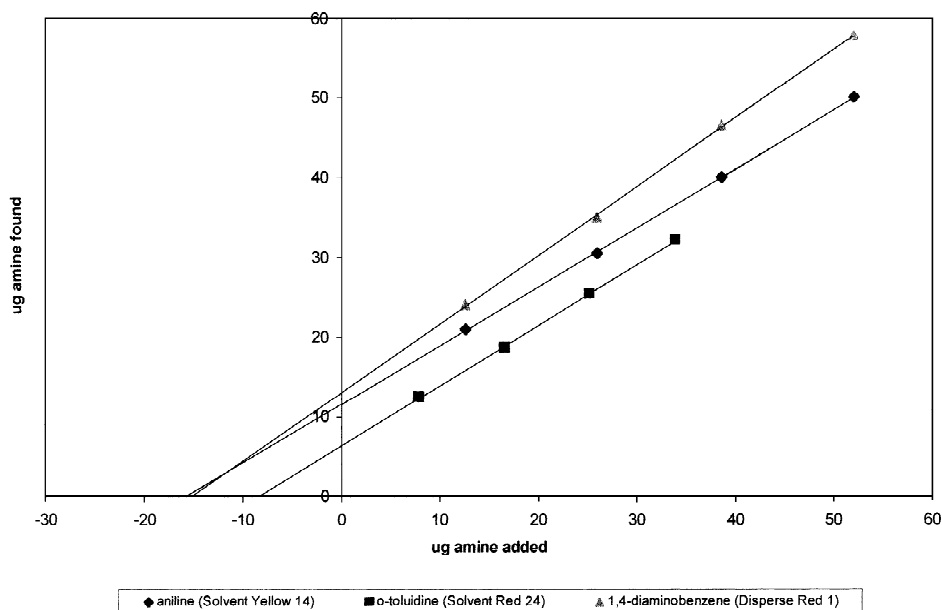


Fig. 5. Standard addition of different quantities of amines in the azo reduction of colorants Solvent Yellow 14, Solvent Red 24 and Disperse Red 1.



obtained in the evaluation of the free amines, except for 1,4-diaminobenzene in Disperse Red 1. In this case, the yield of the total reduction process is lower, which can be consistent with the assumption that maybe some other cleavage products can appear.

#### 4. Conclusions

The use of  $\text{Na}_2\text{S}_2\text{O}_4$  for the cleavage of the  $-\text{N}=\text{N}-$  linkage followed by HPLC analysis of the reduction products allows monitoring and determination of known carcinogenic aromatic amines formed from the reduction of azo-colorants in polymer matrices, and assessment of the risk of toy products. Reduction process was studied by the use of factorial designs and the most significant factors were identified. Time has no apparent influence (even for the diazo dye), temperature being the most significant variable, as well as dit/col ratio. Reduction profiles for each colorant showed that 65 °C, dit/col ratio 10, and 5 min are sufficient for the complete reduction of dyes, where total decoloration of the solutions was observed in every case. The yield of the total reduction process was found to be higher than 80% in every case.

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