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Multisyringe chromatography (MSC) using a monolithic column for the determination of sulphonated azo dyes

Cristina Fernández [a], M. Soledad Larrechi [a], R. Forteza [b], V. Cerdà [b], M. Pilar Callao [a,*]

[a] Department of Analytical and Organic Chemistry, Rovira i Virgili University, Marcel·lí Domingo s/n Campus Sescelades, E-43007 Tarragona, Spain
[b] Department of Chemistry, Faculty of Sciences, University of the Balearic Islands, Carretera de Valldemossa, Km 7.5, E-07122 Palma de Mallorca, Spain

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ABSTRACT

A methodology based on multisyringe chromatography with a monolithic column was developed to determine three sulphonated azo textile dyes: Acid Yellow 23, Acid Yellow 9 and Acid Red 97. An ion pair reagent was needed because of the low affinity between the monolithic column and the anionic dyes. The proposed analytical system is simple, versatile and low-cost and has great flexibility in manifold configuration.

The method was optimized through experimentation based on experimental design methodology. For this purpose two blocks of full factorial 2^3 were done sequentially. In the first experimental plan, the factors studied were: the % of acetonitrile in organic phase, the % of H_2O in the mobile phase and the kind of ion pair reagent. In this stage, a simple configuration was used which has only one syringe for the mobile phase.

After the first experimentation, we added a second syringe with a second mobile phase to the multisyringe module and performed a second full factorial 2^3. The factors studied in this case were: the % of acetonitrile in the second mobile phase, the pH and the concentration of ion pair reagent in both mobile phases. After this design, the optimal conditions were selected for obtaining a good resolution between the peaks of yellow dyes (1.47) and the elution of red dye in less than 8 min.

The methodology was validated by spiking different amounts of each dye in real water samples, specifically, tap water, well water and water from a biological wastewater lagoon.

1. Introduction

Azo dyes are the main category of dyes used in the textile industry and many of them are highly soluble in water and resistant to microbial degradation. Consequently, these compounds can be found in wastewater as well as in surface water [1]. These dyes are of great environmental and toxicological concern, which means that reliable methods are needed for their determination.

The most common methodologies for this purpose use separation techniques [2]. The most frequently applied technique for determining sulphonated azo dyes is ion pairing high-performance liquid chromatography (HPLC) with tetraalkylammonium salts. This technique is used because it fully ionizes anionic (poly)sulphonated dyes over a broad pH range without suppressing their dissociation in buffered mobile phases at a low pH [3–7]. Due to the ionic character of the analytes, electrophoresis has a great potential for determining this kind of compound [8–11]. Also, methodologies have been proposed that employ UV–visible spectrophotometry to make direct measurements; these methodologies have lower experimental costs and lower analysis times. In these cases, to solve the lack of selectivity, chemometric techniques are employed to obtain the concentration of the dyes [12–14]. In spite of their advantages, these kinds of methodologies are not usually used in routine analyses in laboratories.

The aim of our study is to develop a methodology using multisyringe ion pair chromatography with a monolithic column to determine three sulphonated azo dyes (Acid Yellow 23, Acid Yellow 9 and Acid Red 97) which are used jointly in the textile industry to obtain certain tonalities.

Monolithic columns offer the opportunity to perform separations in some flow-analysis manifolds that would not withstand the back-pressure from conventional packed columns. Monolithic columns are more tolerant of eluent switching and equilibrate more rapidly, which means they can work in multiisocratic mode. The applications of ion chromatography and ion pair chromatography with C18 monolithic columns have been reviewed [15]. It has to be noticed that despite their advantages this kind of columns are not frequently used in typical HPLC configurations.

Sequential injection chromatography (SIC) used with a hybrid FIA/HPLC system with monolithic columns combines chromato-

* Corresponding author. Tel.: +34 977558199; fax: +34 977558446.
E-mail addresses: mariapilar.callao@urv.cat, callao@quimica.urv.es (M.P. Callao).

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graphic techniques with the flow techniques of analysis and has been shown to be a good alternative to HPLC for quickly analyzing simple samples [16,17]. There are some examples in the literature that use SIC to determine pharmaceutical compounds [18–20], pesticides [21] or phenolic species [22]. Multisyringe chromatography (MSC) is a new combination of multisyringe flow injection analysis with low pressure chromatography, which allows the mobile phase to be managed in ways that are not possible with SIC. The main difference between SIC and MSC is that in SIC only one syringe is employed; this means that there can be only one mobile phase. In MSC, a multisyringe module is used which makes the system more versatile and allows to use more than one mobile phase in the process, as well as sample injection and derivatization strategies. Other features of the multisyringe module are its robustness and the use aggressive fluids [23]. MSC has been used to determine different analytes such vitamins [24], phenolic pollutants [25], pharmaceutical residues [26,27].

In chromatographic processes, a large number of factors could be influential when separating analytes. Experimental designs are useful for optimizing processes involving a high number of factors [28]. In most of the papers consulted, the optimal conditions for separating the dyes were obtained by varying one factor at a time without taking into account the possible interactions between factors. Recently, experimental designs have been proposed for use in HPLC [29–32], but have only been used to optimize SIC or MSC methodologies in a few cases [24].

After determining the acceptable initial conditions that allow the elution of the three dyes, we have used experimental design methodologies to find the optimal conditions for separating these three dyes. The usual strategy, when there is an elevated number of factors to consider, is to design an experiment to screen the various factors (Plackett–Burman or saturated fractionated factorial designs), these being the methodologies with the lowest experimental cost. Moreover, in these strategies it must be assumed that the interactions between two or more factors have no effect on the response. Consequently, these kinds of designs can lead to erroneous conclusions.

Confusion between the factors and the interactions can be avoided by optimizing the process through the performance of sequentially different full factorial designs. This experimentation determines the effect of each factor and each interaction. In this case a first full factorial design is built which contains 3 or 4 of the most basic factors. On the basis of the results obtained from this first design, a second design is constructed which uses other factors or which rescales some of the factors because they may have varied over inappropriate ranges.

To our knowledge, no studies have yet reported the use of SIC or MSC methodologies to determine sulphonated azo dyes.

2. Experimental

2.1. Apparatus

The proposed multisyringe liquid chromatography (MSC) system (Fig. 1) used a multisyringe burette module (MSP; CRISON, Alella, Spain), equipped with two 5 ml high precision bidirectional syringes and one additional MTV-3-N1/4UKG solenoid valve (Takasago, Japan) that can endure pressures of up to 600 kPa without damage. The manifold was constructed with 0.8 mm i.d. poly(tetrafluoroethylene) (PTFE) tubing. The chromatographic separation was done on a Phenomenex Onyx Monolithic C18 silica-based monolithic column (25 mm × 4.6 mm) protected with a guard cartridge Phenomenex Onyx C18 (5 mm × 4.6 mm). A Hewlett Packard 8453 diode array spectrophotometer equipped with a flow-through quartz cell (Hellma, 18 μl inner volume, 10 mm path length) was used as detector. Measurements were recorded from 220 to 720 nm, with correction at 720 nm in order to minimize the effect of changes in the refractive index (Schlieren effect). The sample volume was 50 μl.

The software package AutoAnalysis 5 (Sciware, Spain) was used to control the instruments, to obtain the data and to process the chromatographic results. Statistical calculations have been performed by MS-Excel.

2.2. Reagents and samples

Acid Yellow 23 and Acid Yellow 9 were purchased from Sigma–Aldrich. Acid Red 97 was obtained from Trumpler Española, S.A. (Barberà del Vallès, Barcelona, España). Fig. 2 shows the molecular formula and the spectra at 30 mg l^{-1} for each dye. All dyes were used without further purification. Stock solutions of 500 mg l^{-1} were prepared in distilled water purified by passage through a Millipore system. Methanol Chromasolv® (HPLC grade, Sigma–Aldrich) and acetonitrile (HPLC-gradient grade PAI-ACS, Panreac) were used to prepare the required mobile phase. Other chemicals (acid orto-phosphoric and di-ammonium hydrogen phosphate) were obtained from Scharlau (Barcelona, Spain). Triethylamine hydrochloride and dodecyltrimethylammonium bromide were used as ion pair reagents and were obtained from Fluka and Across Organics respectively.

Mobile phases were filtered through 0.45 μm Nylon membranes. Calibration standards and samples were filtered through 0.45 μm Teflon syringe filters. We used Teflon filters instead of Nylon filters to prevent the sulphonated azo dyes from adsorbing in the filters. Mobile phases as well as standards and samples were degassed for 10 min in an ultrasonic bath. Spiked samples were prepared in tap water, well water and lagoon water from a biological wastewater treatment station.

2.3. Procedure

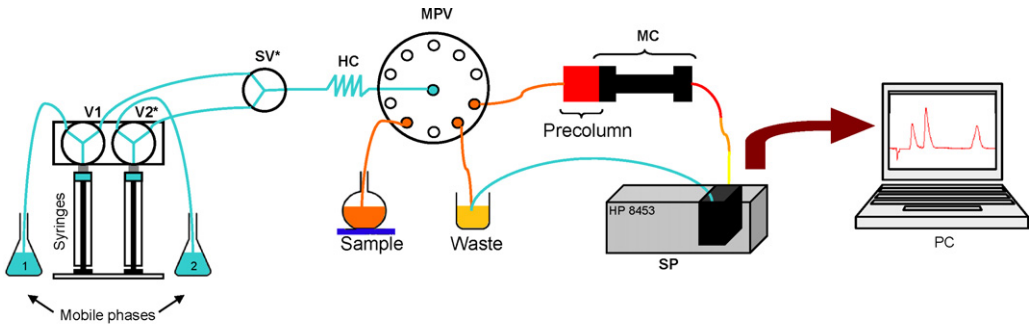
2.3.1. Chromatographic aspects

Usually the chosen mobile phase in ion pairing chromatography is water/methanol, but methanol can cause overpressure problems with the monolithic column due its high viscosity (0.59 cP at 25 °C, compared with 0.38 of acetonitrile or 0.894 cP of water), for this reason we used a mixture of acetonitrile/methanol as the organic part in the mobile phase in order to decrease the viscosity. We use a phosphate buffer (acid orthophosphoric and di-ammonium hydrogen phosphate) in order to control the pH of the mobile phase.

An ion pair reagent is needed to retain the compounds because of their ionic character and their low affinity with the C18 monolithic column. We have studied how the dye retention behaves with different amounts of a small ternary ammonium salt (triethylamine hydrochloride) and a voluminous quaternary ammonium salt (dodecyltrimethylammonium bromide).

Before starting the analysis of the factors with the experimental design, certain variables were fixed that were thought not to have a determinant effect on dye separation. Thus, the sample volume was fixed at 50 μl because this provides enough sensitivity to determine the dyes and because smaller volumes are less reproducible when a multisyringe is employed to inject the sample. The flow rate was fixed at 1 ml min^{-1}. Major fluxes produce problems of overpressure when the proportion of methanol is increased in the mobile phase.

Every day the column and precolumn were preconditioned with 5 ml of a 0.01% triethylamine solution in water to prevent the dyes irreversibly adsorbing to the residual silanol groups on the bonded silica surface [3].



V1 and V2: Syringe valves; SV: external solenoid valve; HC: holding coil of 3 ml capacity; MPV: multiposition valve; Precolumn (5 x 4.6 mm); MC: Monolithic column (25 x 4.6 mm); SP: Spectrophotometer.

* V2 and SV are added to the system when a second phase mobile is necessary.

Fig. 1. Multisyringe chromatography (MSC) system.

2.3.2. Experimental design aspects

First, a 2^3 full factorial experimental design was built, in which the factors considered were the percentage of acetonitrile in the organic phase, the percentage of aqueous phase in mobile phase and the type of ion pair reagent. Multisyringe chromatography (MSC) with only one syringe and mobile phase were used because this is the simplest configuration.

The results obtained in the first experimental design showed that a second mobile phase was needed to elute red dye in a shorter time; for this reason a second syringe was added to the multisyringe with the aim of dispensing this second mobile phase. We decided to use a multiisocratic mode instead of a gradient mode due to the different composition of the two mobile phases. A second 2^3 full factorial design was created which included new factors as well as the most influential factors of the first design. Together these were the % of acetonitrile in mobile phase, the pH and the concentration of ion pair reagent. This design was used to finally select the best conditions for separating the three dyes.

In all the experiments of both experimental designs, a standard 10 mg l^{-1} solution of each dye was injected in the system. The chromatograms were showed at $\lambda = 460$ nm because at this wavelength, all of the studied dyes gave a signal with a correction wavelength of 720 nm that minimized the effect of changes in the refractive index (Schlieren effect).

2.3.3. Quantitative analysis

In order to establish a calibration curve, 10 different standards were prepared in milli-Q water using different concentrations of each dye in each sample (5–50 mg l^{-1}). In this case the wavelength of maximum sensitivity for each dye (392 nm for Acid Yellow 9, 428 nm for Acid Yellow 23, 500 nm for Acid Red 97) was used for quantification. The peak area was used as the analytical signal. Each dissolution was repeated twice and an ANOVA regression test was used to validate the resulting calibration curve [33]. The concentration values of the calibration standards are shown in the first 10 rows of Table 1. As can be seen, different concentrations of each dye have been selected in each standard, all within the linearity range, because the calibration curves include all possible circumstances, for example, dyes that are present in the same concentrations or dyes that are present in high or low concentrations. Repetitions of standard 1, which corresponds to the standard containing 10 mg l^{-1} of each dye, were done at different days in order to calculate the reproducibility and repeatability of the methodology.

All calibration standards were prepared from a concentrated standard of 500 mg l^{-1} of each dye in milli-Q water, the corresponding solutions being diluted with the first mobile phase used in the corresponding elution.

In order to validate the method, we used spiked real water samples (tap water, well water and lagoon biological wastewater).

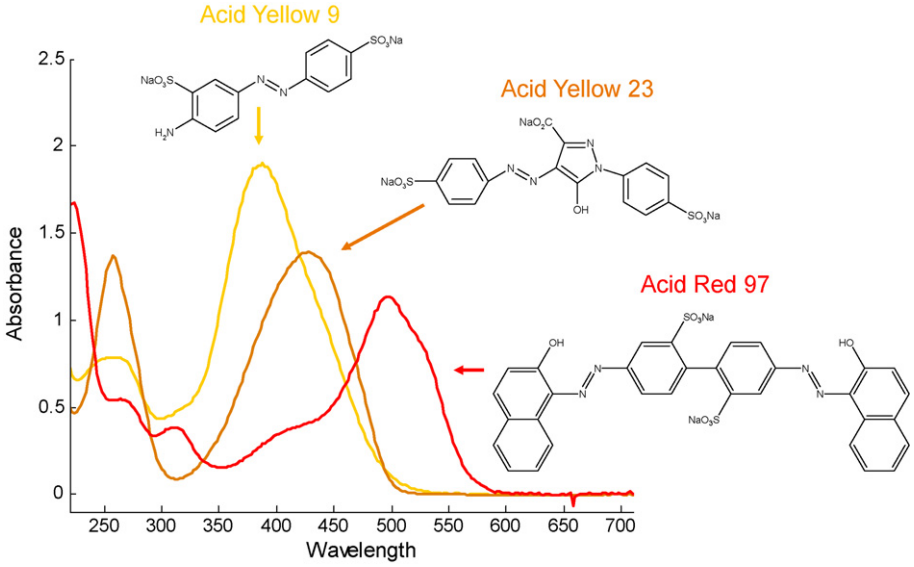


Fig. 2. Spectra and molecular formula of the studied dyes.

Table 1
Concentration of calibration standards and real samples (mg l^{-1}).

Number	Acid Yellow 9	Acid Yellow 23	Acid Red 97
1	10	10	10
2	40	20	20
3	10	5	40
4	30	30	10
5	20	40	25
6	5	5	50
7	10	40	5
8	50	30	40
9	25	25	30
10	30	50	20
S1[a]	20	35	20
S2[a]	25	10	10
S3[a]	10	15	25

[a] Spiked concentration in real water samples.

These samples were prepared in the same way as the standards, that is, different quantities of each dye were spiked in each kind of water sample instead of in milli-Q water. The real water was checked beforehand to ensure it did not contain any of the studied dyes. The spiked concentrations in the real samples are shown in the last three rows of Table 1. The concentration levels selected are in according to the dye concentrations obtained in industry during and after the tanning process. Usually, these concentrations are higher from 30 to more than 100 mg l^{-1} [13] and a dilution step is necessary before analytical determination.

3. Results

3.1. Experimental design

As has been stated, the first experiments were carried out using only one syringe in the multisyringe module working in isocratic mode. The factors studied in the first full factorial design were the percentage of water in the mobile phase, the percentage of acetonitrile in the organic phase formed by methanol and acetonitrile and the type of ion pair reagent (dodecyltrimethylammonium bromide or triethylamine hydrochloride). All of the experiments were carried out at pH = 7.5. The responses studied were qualitative (separation or not of the two yellow dyes and elution or not of red dye).

Table 2 shows the 8 experiments in this 2^3 experimental design. It can be seen that triethylamine hydrochloride as ion pair reagent does not allow to separate yellow dyes; instead, it is necessary to use dodecyltrimethylammonium bromide to favor the retention of these dyes in the monolithic column. Regarding experiments 3 and 4 in Table 2, it can be seen that when the mobile phase contains 50% H_2O, 50% acetonitrile (100% of acetonitrile in organic phase) and DTMA, the yellow dyes are not separated but the red dye is eluted; however, when the mobile phase contains 70% H_2O, 30% acetonitrile (100% of acetonitrile in organic phase) and DTMA, the yellow dyes are completely separated but the red dye is not eluted. These results suggest that an intermediate mobile phase could separate yellow dyes and elute the red dye. We tested this hypothesis by using a mobile phase mixture of 60% H_2O and 40% acetonitrile (100% of acetonitrile in organic phase) and keeping dodecyltrimethylammonium bromide as the ion pair reagent; however, under these conditions the yellow dyes were not separated and the red dye were not eluted.

The main conclusion of this additional experiment was that the mobile phases which allow the two yellow dyes to be separated are different from the mobile phases which elute the red dye in a reasonable time. This means that the dyes studied cannot be separated or eluted in a reasonable time if only one syringe or mobile phase is used. The use of multisyringe chromatography (MSC) allows two syringes to be used, that is, two mobile phases working in multisocratic mode. First, we can employ one mobile phase to separate the two yellow dyes and then another different mobile phase to elute the red dye without stabilization between the two phases because monolithic columns are more tolerant of eluent switching and equilibrate more rapidly than the particle-packed columns used in HPLC.

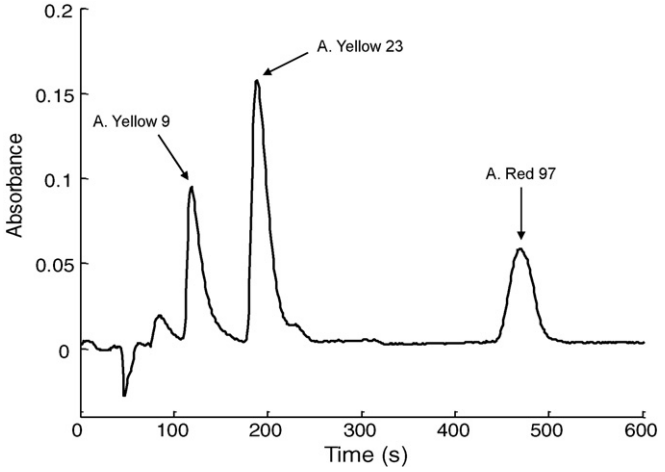


Fig. 3. Chromatogram obtained with the optimal conditions.

In order to find the optimum conditions, a second full factorial 2^3 design was performed. According to the results obtained in the previous step, the initial factors were fixed as follows: 50% water, 25% acetonitrile and 25% methanol in the first mobile phase and dodecyltrimethylammonium bromide as the ion pair reagent. The factors studied in this case were the % of acetonitrile in mobile phase 2 formed by a mixture of water/acetonitrile, the pH of both mobile phases, and the concentration of ion pair reagent in both mobile phases. This second design is described in Table 3, which shows the experimental plan in its three first columns and the quantitative responses obtained (the resolution between two peaks corresponding to yellow dyes and the analysis time) in its last two columns.

This experimental design allowed us to select the best conditions for separating and determining these dyes. Table 3 shows that experiments 5 and 7 give good resolution values between the peaks corresponding to yellow dyes and the analysis time is similar in both experiments. Any of these experiments could be used to separate the three dyes but in our case we chose experiment 5 because it has the highest resolution value between the two first peaks, specifically 1.47, and because the red dye was eluted in a shorter analysis time, specifically 468 s. A chromatogram obtained from this experiment is shown in Fig. 3. This figure shows that the three dyes could be completely and perfectly separated in less than 8 min. The first dye to elute to the monolithic column is Yellow 9, followed by Yellow 23 in second place and Acid Red 97 last of all.

The operating sequence for multisyringe liquid chromatographic separation is summarized in Table 4, where details of multisyringe burette motion, positions of the selection valve, syringe valves and the external solenoid valve are given along with the corresponding consumption of the mobile phases and the sample.

3.2. Calibration and validation in real samples

Table 5 shows the figures of merit for the calibration curves obtained for each dye. All of the curves pass the ANOVA regression test. The detection limit was calculated with 95% of confidence

Table 2
Experimental plan and responses of the first experimental design 2^3.

Experiment	H_2O	% ACN in organic phase[a]	Ion pair reagent	Separation of yellow dyes	Presence of red dye peak
1	50	50	DTMA	Yes	No
2	70	50	DTMA	No	No
3	50	100	DTMA	No	Yes
4	70	100	DTMA	Yes	No
5	50	50	TEA	No	Yes
6	70	50	TEA	No	No
7	50	100	TEA	No	Yes
8	70	100	TEA	No	Yes

DTMA = dodecyltrimethylammonium bromide; TEA = triethylamine hydrochloride.
[a] Organic phase = methanol and acetonitrile.

Table 3
Experimental plan and responses of the second experimental design 2^3.

Experiment	% ACN in phase 2	pH	Ion pair concentration (mM)	Resolution between yellow dye peaks	Retention time of red dye (s)
1	50	4	5	0.78	345
2	70	4	5	0.29	234
3	50	7.5	5	0.29	357
4	70	7.5	5	0.44	242
5	50	4	15	1.47	468
6	70	4	15	1.14	256
7	50	7.5	15	1.34	487
8	70	7.5	15	1.04	244

Table 4
Operating sequence for MSC separation.

	Operation	Flow rate (ml min^{-1})	V1	V2	VS	Observations
MSP	Dispense 4000 μl	1	On	Off	Off	Pre-conditioning of the system
SP	Measure blank					
MSP	Aspirate 3000 μl	2.5	Off	Off	Off	
MPV	Move to position 8					
MSP	Aspirate 200 μl	2.5	On	Off	Off	Loading of sample
MPV	Move to position 3					
MSP	Dispense 1000 μl	2.5	On	Off	Off	
MSP	Aspirate 1750 μl	2.5	Off	Off	Off	
MPV	Move to postion 8					
MSP	Aspirate 50 μl	1	On	Off	Off	
MPV	Move to position 1					
SP	Get spectral range from 220 to 720 nm					Data acquisition
MSP	Multicommutation protocol HC[a]	1	On	Off	Off	
	500 μl phase 1 + 9500 μl phase 2	1	Off	On	On	
SP	Stop measurement					

V1: Syringe valve corresponding to mobile phase 1; V2: syringe valve corresponding to mobile phase 2; VS: external solenoid valve; MSP: multisyringe pump; MPV: multiposition valve; SP: spectrophotometer; position 8 corresponds to the sample; position 3 corresponds to waste; position 1 corresponds to monolithic column.
[a] HC: holding coil contains 3 ml of phase A.

Table 5
Figures of merit for the calibration curves of each dye.

	Acid Yellow 9	Acid Yellow 23	Acid Red 97
Interval range (mg l^{-1})	5–50	5–50	5–50
Wavelength	392	428	500
Slope (sd[a])	0.55 (0.01)	0.43 (0.01)	0.30 (0.01)
Intercept (sd[a])	0.69 (0.28)	0.01 (0.29)	0.04 (0.20)
Standard deviation of residuals	0.64	0.65	0.43
r	0.9969	0.9954	0.9957
n	20	20	20
ANOVA, F_{cal}[b]	1.48	2.41	2.38
Detection limit (mg l^{-1})	1.75	2.30	2.19
Reproducibility[c] (RSD%, 10 mg l^{-1})	4.0	2.7	3.3
Repeatability[d] (RSD%, 10 mg l^{-1})	3.7	2.4	3.0

[a] sd: standard deviation.
[b] $F_{tab}(0.05,8,18) = 3.03$.
[c] 8 days.
[d] 10 repetitions.

whilst taking into account the uncertainty in the regression line [33]. The repeatability, as a standard deviation, was evaluated by performing ten replicate measurements in a mixture of 10 mg l^{-1} of each dye. Reproducibility was calculated as the standard deviation of a solution with 10 mg l^{-1} of each dye on 8 different days (3 replicates per day). The values of reproducibility and repeatability are satisfactory taking into account the simply configuration employed (a syringe) to inject the sample.

To validate this methodology in real samples, we used tap water, well water and lagoon biological wastewater spiked with different concentrations of the selected dyes. Specifically, we determined these dyes in nine samples, three for each kind of water, spiked with different concentrations of Acid Yellow 9, Acid Yellow 23 and Acid Red 97 (see Table 1).

In order to validate the results obtained with the real samples a regression line was established representing the spiked concentrations versus the concentrations predicted with the MSC methodology. This line was then compared using a join test with the following line of identity: regression slope = 1, regression intercept = 0 [33].

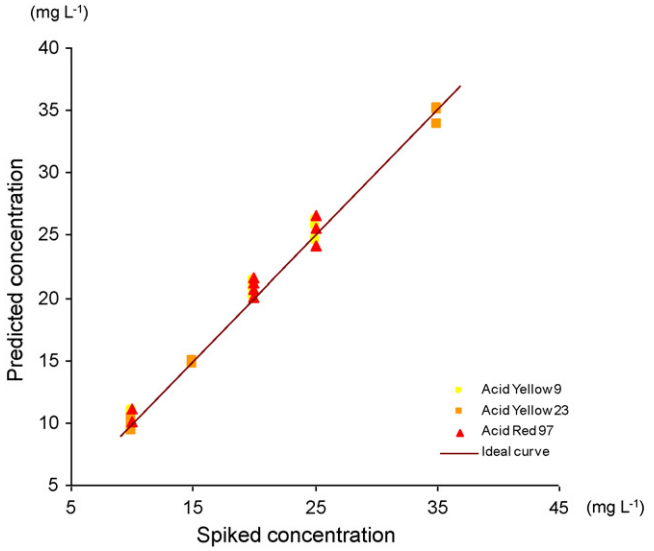


Fig. 4. Validation curve for well water samples.

All the dyes passed the test for all the water samples with a significance level of $\alpha = 0.05$, except Acid Yellow 23 in lagoon biological wastewater, which passed the test with a significance level of $\alpha = 0.015$. Fig. 4. shows the spiked concentration versus the predicted concentration of the studied dyes in the well water samples.

4. Conclusions

The proposed MSC system is simpler, more versatile and cheaper than HPLC when the samples are fairly simple, as is the case in our study. It can be regarded as a low pressure alternative to HPLC and it could be a very attractive technique for improving selectivity in flow analytical systems (FIA and SIA). Moreover, back-pressure was not a limiting factor in MSC.

MSC allowed us to use similar flow-rates to those in HPLC under the same conditions. Therefore, special benefit can be derived from combining flow techniques with monolithic columns when carrying out low-cost chromatographic separations of azo dyes in polluted water samples. Another significant advantage of using MSC is its great flexibility in manifold configuration. If necessary in the future, an on-line pretreatment of the sample can be carried out using a multisyringe with a solid phase extraction cartridge to extract and preconcentrate sulphonated azo dyes from water samples.

The application of experimental designs allowed us to use a smaller number of experiments and qualitative responses to optimize the separation of the three sulphonated azo dyes (Acid Yellow 9, Acid Yellow 23 and Acid Red 97). The use of this strategy can determine the influence of each factor (pH, mobile phase, ion pair reagent, etc.) and thus simplify the experiment because the separation behaviour could be predicted when the value of the factors is changed. This provides a collection of quality chromatograms that can be used for the further quantification of the analytes.

Using the experimental design has clearly proven that the three target compounds cannot be separated with one single syringe or mobile phase. These compounds can, nevertheless, be completely separated using ion pair multiisocratic MSC with two mobile phases. This methodology has been validated in real samples (tap water, well water and water from a lagoon in a biological wastewater treatment station) and in all cases good results were obtained.

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