



Membrane filtration of Sudan orange G on a cellulose acetate membrane filter for separation–preconcentration and spectrophotometric determination in water, chili powder, chili sauce and tomato sauce samples

Zeid A. ALOthman^a, Yunus E. Unsal^b, Mohamed Habila^a, Azza Shabaka^c, Mustafa Tuzen^b, Mustafa Soylak^{d,*}

^a Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

^b Gaziosmanpasa University, Fac. of Science and Arts, Chemistry Dept., 60250 Tokat, Turkey

^c High Institute of Public Health, Environmental Health Department, Alexandria University, Egypt

^d Erciyes University, Faculty of Science, Department of Chemistry, 38039 Kayseri, Turkey

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ABSTRACT

A simple membrane filtration procedure for separation–enrichment of Sudan orange G is presented. The method is based on the adsorption of Sudan orange G on a cellulose acetate filter and its elution from the membrane with 10 mL of ethanol. Sudan orange G in the eluent was determined by UV–visible spectrophotometry at 388 nm. The effect of analytical conditions, including pH, flow rates and eluent, sample volume, type of membrane for quantitative preconcentration and separation of Sudan orange G were examined. The influences of matrix components on Sudan orange G recoveries were studied. The preconcentration factor was 125. The detection limit was $4.9 \mu\text{g L}^{-1}$. The relative standard deviation was 4.3%. The presented procedure was applied to chili powder, chili sauce, tomato sauce, powdered beverage and water samples.

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1. Introduction

Synthetic dyes used in various industries, including food, textile, and petroleum, are potential pollutants for food and environmental samples, in particular natural water samples. Sudan dyes are a class of azo dyes. They have been illegally used as additives in food products to maintain their red–orange color and thus stimulate sales of these products in the market (Qiao et al., 2011; Rebane et al., 2010; Sun et al., 2007; Soylak et al., 2011a,b; Stiborova et al., 2002). Sudan dyes are thought to be carcinogenic yet have been determined as a contaminant in chili powder (Calbani et al., 2004; Liu et al., 2007).

Instrumental methods have been used for the identification and determination of various food colorants including Sudan Dyes, like spectrophotometry, high performance liquid chromatography, thin-layer chromatography, gas chromatograph and capillary electrophoresis, (Katerina et al., 2007; Ghaedi et al., 2011; Saad et al., 2011; Pourreza et al., 2010; Biparva et al., 2010; Wang et al., 2008; Jaina et al., 2007; Shiri et al., 2011; Tan et al., 2010; Pan et al., 2010). UV–visible spectrometry is an also important technique on the determination of food colorant, because it is simple and low cost. Two important limitations in UV–visible spectrometric

determinations of food colorants arise when levels of analytes are lower than the quantitation limits of UV–visible spectrometry and where there are influences of the concomitants on the signal of colorants (Pourreza et al., 2010).

Various separation–enrichment procedures, including solvent extraction, adsorption, microextraction and cloud point extraction have been used to solve these problems on the determination of analytes (Soylak et al., 1996, 1997; Soliman and Ahmed 2009; Kazi et al., 2009; Khan et al., 2011). They should provide a high enrichment factor and should be suitable for use in routine analysis and be simple, rapid, and cheap (Soylak et al., 1993; Duran et al., 2011; Aydin and Soylak 2007; Xiang et al., 2009; Soylak et al., 2002).

Membrane filtration technique has generally these properties as a separation–enrichment method (Soylak et al., 2007; Narin and Soylak 2003; Chen et al., 1998). Various membrane filters have been used for enrichment and separation of traces organic species, some anions, and metallic species (Soylak et al., 2010; Karatepe et al., 2002; Itoh et al., 1996). In the membrane filtration technique, adsorbed analyte species were eluted from membrane filter; this is one of the advantages of the presented method, because membrane could be used next time.

In presented work, a separation–enrichment procedure for an azo dye that is Sudan orange G in real samples including chili powder, chili sauce, tomato sauce, powdered beverage and water samples

* Corresponding author. Fax: +90 352 4374933.

E-mail addresses: msoylak@gmail.com, soylak@erciyes.edu.tr (M. Soylak).

has been established for use prior to its spectrophotometric determinations. The optimal analytical parameters were examined.

2. Experimental

2.1. Apparatus

A Hitachi 150–20 UV–vis spectrophotometer with a 1.0 cm quartz cell was used. The wavelength was set at 388.0 nm for measurements of Sudan orange G. pH measurements were done by using Sartorius PT-10 Model pH meter with glass-electrode. A filtering flask with a ground stopper was used for filtering to the all model and real solutions.

2.2. Reagents and solutions

All chemicals and reagents used were of analytical reagent grade and were used. Reverse osmosis purified water was used. All glassware was kept overnight in a 10% v/v HNO_3 and then rinsed with water.

Sudan orange G dye (2,4-dihydroxyazobenzene, 4-(phenylazo) resorcinol) was purchased from Sigma–Aldrich Co. (St. Louis USA). A $1 \times 10^{-3} \text{ mol L}^{-1}$ Sudan orange G was prepared in ethanol and stored at 4 °C in the dark. A calibration curve was established using the standard solutions by dilution from $1 \times 10^{-3} \text{ mol L}^{-1}$ Sudan orange G. Cellulose acetate membrane filters were obtained from Osmonics (Westborough, MA). The buffer solutions given by Soy lak et al., (1999) were used in the presented work.

2.3. Model procedure

25 mL of each aqueous sample solution containing $1 \times 10^{-5} \text{ mol L}^{-1}$ Sudan orange G was prepared in a beaker. 10 mL of the buffer solutions was added to provide the desired pH values between 2.0 and 7.0. After 10 min, Sudan orange G solution was passed through cellulose acetate membrane filter (0.45 μm pore size, 47 mm in diameter) by filtration under suction with an aspirator. Sudan orange G retained on the membrane filter was eluted with 10 mL of ethanol. Sudan orange G content of eluent was determined by UV–vis spectrophotometer at 388.0 nm.

2.4. Applications to food and water samples

One g each of sample purchased from a local market, were dissolved in 30 mL of hot water (75 °C). After cooling, the pH of the samples was adjusted to 4.0 using acetate buffer. The procedure described above was then applied. Blank samples were also analyzed.

The water samples ($N = 3$) from Nigde Bor Spring were placed in a beaker and adjusted to pH 4.0, followed by the procedure was applied given above.

3. Results and discussion

3.1. Effect of pH

The effect of pH on the recovery of Sudan orange G on a cellulose acetate membrane filter was studied over the pH range of 2.0–7.0. The results for pH works are depicted in Fig. 1. The recovery values for Sudan orange G was quantitative in the pH range of

Table 1
Effects of eluents ($N = 3$).

Eluent	Recovery (%)
Acetonitrile (10 mL)	82 ± 2
Propanol (10 mL)	75 ± 2
Acetone (10 mL)	79 ± 3
Methanol (10 mL)	96 ± 2
Ethanol (5 mL)	78 ± 2
Ethanol (10 mL)	96 ± 1
Ethanol (15 mL)	100 ± 1
DMF (10 mL)	94 ± 1
DMS (10 mL)	95 ± 1
1 M NaOH (10 mL)	35 ± 2
1 M HNO_3 (10 mL)	28 ± 2
40% acetonitrile/60% acetate buffer (10 mL)	36 ± 2
60% acetonitrile/40% acetate buffer (10 mL)	35 ± 2
80% acetonitrile/20% acetate buffer (10 mL)	28 ± 1
40% acetonitrile/60% phosphate buffer (10 mL)	40 ± 2
60% acetonitrile/40% phosphate buffer (10 mL)	41 ± 2

3.0–5.0. All further works were performed at pH 4.0 by using an ammonium acetate/acetic acid buffer.

3.2. Elution studies

The effects of various eluents, given in Table 1, on elution of Sudan orange G from cellulose acetate filter were studied. The quantitative recovery values for Sudan orange G were obtained using 10 mL of ethanol, methanol, dimethyl sulfide and dimethylformamide. The recovery values were not quantitative with the other eluents. Therefore, 10 mL of ethanol was chosen for further studies.

3.3. Flow rates

The effects of flow rates of sample and eluent on the recovery values of Sudan orange G from cellulose acetate filter were investigated over the flow rate range 1–8 mL min^{-1} . The results are shown in Figs. 2 and 3. Sudan orange G was quantitatively adsorbed and desorbed, respectively, over the sample flow rate range 1–6 mL min^{-1} and the eluent flow rate range 1–3 mL min^{-1} . In subsequent work, 5 and 3 mL min^{-1} were preferred as flow rates of the sample and eluent, respectively.

3.4. Sample volume

Sample volume is an important factor enrichment studies to obtain high preconcentration factors (Elci et al., 2000; Soy lak et al.,

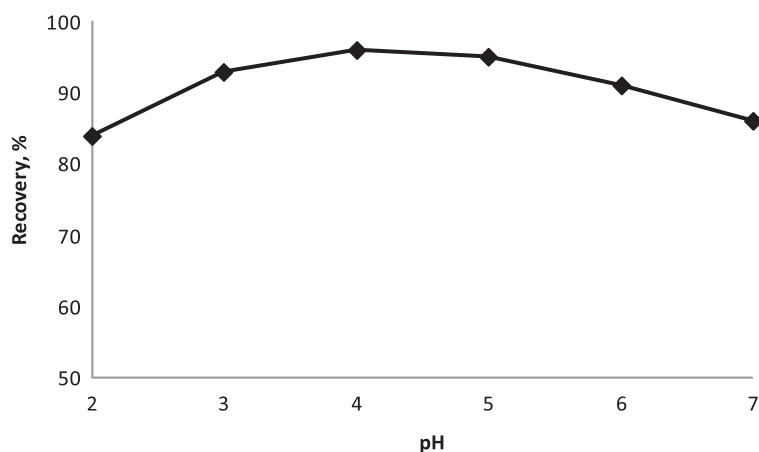


Fig. 1. The influences of pH on recovery of Sudan orange G ($N = 3$).

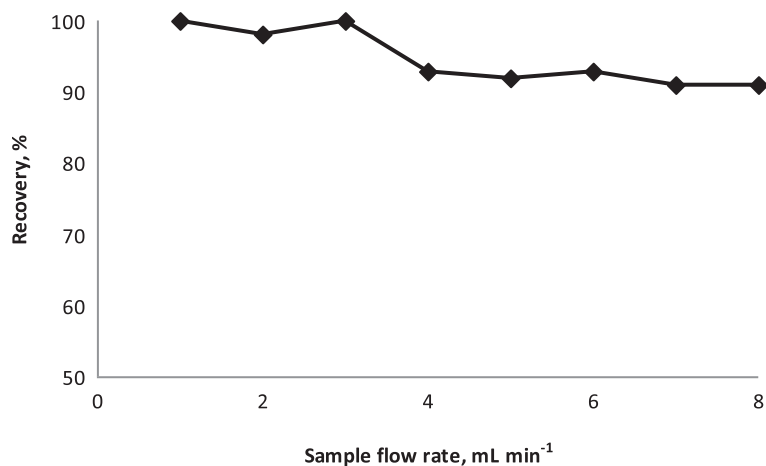


Fig. 2. Effect of flow rate of sample on recovery of Sudan orange G (N = 3).

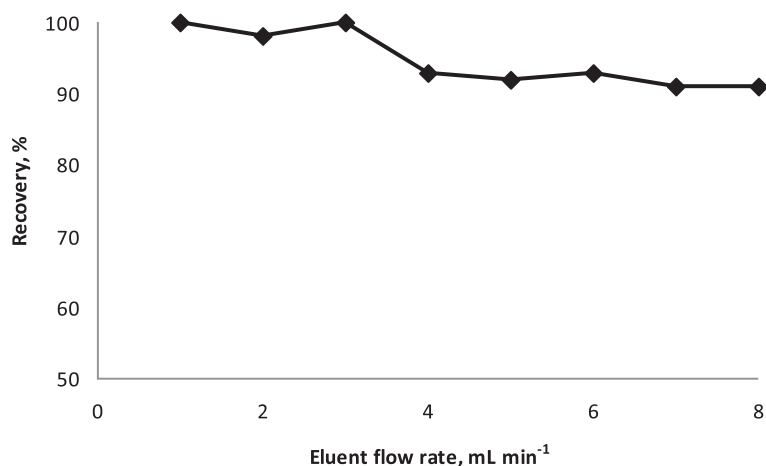


Fig. 3. Influences of flow rate of eluent on recovery of Sudan orange G (N = 3).

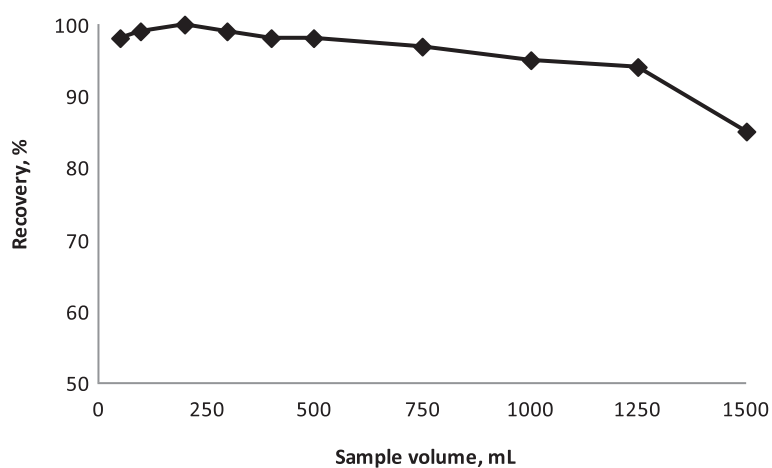


Fig. 4. Sample volume-recovery relations (N = 3).

2007, 2011a,b; Afzali et al., 2010). The influence of volume of sample was examined over the range 50–1500 mL. Sudan orange G recoveries were quantitative ($\geq 95\%$) below 1250 mL (Fig. 4). Above 1250 mL, recoveries were below 90%. The factor of preconcentration was calculated as 125 when the sample volume is 1250 mL while eluent volume is 10 mL.

3.5. Reuse of filter

The influences of repeated use of cellulose acetate membrane on the recoveries of Sudan orange G was investigated. The results are summarized in Table 2. Membrane filter could be used eight times for enrichment experiments.

Table 2

The influences of number of uses of membrane on the recoveries of Sudan orange G.

Usage number	Recovery (%)
1	99 ± 2
2	100 ± 1
3	98 ± 1
4	98 ± 1
5	97 ± 1
6	96 ± 2
7	95 ± 2
8	96 ± 1
9	89 ± 2
10	82 ± 2

Table 3Matrix effects on the recovery of Sudan orange G ($N = 3$).

Matrix components	Added as	Concentration (mg L ⁻¹)	Recovery (%)
Mg ²⁺	MgCl ₂	5000	95 ± 1
Na ⁺	NaCl	15000	99 ± 1
K ⁺	KCl	5000	96 ± 2
Cl ⁻	NaCl	20000	99 ± 1
SO ₄ ²⁻	Na ₂ SO ₄	3000	96 ± 2
Pb ²⁺	Pb(NO ₃) ₂	100	95 ± 3
Cu ²⁺	Cu(NO ₃) ₂ ·3H ₂ O	100	95 ± 1
Fe ³⁺	Fe(NO ₃) ₃ ·9H ₂ O	100	94 ± 2
Zn ²⁺	Zn(NO ₃) ₂ ·6H ₂ O	50	97 ± 2
Ni ²⁺	Ni(NO ₃) ₂ ·6H ₂ O	50	100 ± 1
Co ²⁺	Co(NO ₃) ₂ ·3H ₂ O	50	94 ± 2
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	30	96 ± 2
Cd ²⁺	Cd(NO ₃) ₂ ·4H ₂ O	30	97 ± 1
Caramel		8	98 ± 2
Pea green		10	94 ± 1
Allura red		5	96 ± 2
Rhodamine B		5	97 ± 1
Sunset yellow		8	98 ± 2
Pararosaniline		8	95 ± 1
Tatrazine		10	94 ± 1

3.6. Type of filter

Various types of membrane filters were performed to investigate their influence on the recovery of Sudan orange G. Quantitative recoveries of Sudan orange G were obtained with cellulose acetate membrane. The recoveries of Sudan orange G were 71 and 81% using cellulose nitrate and polysulfone membrane filters, respectively.

3.7. Matrix effects

The influences of matrix components of real samples on the recovery values of Sudan orange G on cellulose acetate filter were studied. The results are summarized in Table 3. The limit of

Table 5Spike studies to Nigde Bor spring water ($N = 3$).

Nigde Bor spring water		
Added (μg L ⁻¹)	Found (μg L ⁻¹)	Recovery (%)
0	BDL	–
250	249 ± 4	99
500	500 ± 13	100
750	742 ± 21	99

BDL, below the detection limit.

Table 6Sudan orange G content of chili powder, chili sauce and tomato sauce ($N = 3$).

Samples	Sudan orange G (μg g ⁻¹)
Chili powder 1	774 ± 18 ^a
Chili powder 2	998 ± 21
Chili powder 3	165 ± 5
Chili powder 4	193 ± 7
Chili sauce	925 ± 19
Tomato sauce 1	119 ± 4

^a Mean ± standard deviation.

tolerance of matrix ions was taken as that value which caused an error of less than ± 5%.

3.8. Figure of merits

The detection limit (LOD) of the presented method was studied under optimal experimental conditions by using blank solutions. LOD, defined as the concentration equivalent to 3 times the standard deviation ($N = 10$) of a reagent blank was calculated as 4.9 μg L⁻¹. A regression equation for the calibration curve was linear in the range of 1×10^{-7} to 5×10^{-4} mol L⁻¹, $A = 0.4583C - 0.0035$ (C , concentration, A , absorbance), $r^2 = 0.9998$. The relative standard deviation (RSD) ($N = 10$) was 4.3%.

In order to get some information on the accuracy of the procedure, different amounts of Sudan orange G were spiked to dissolved real samples including chili powder, tomato sauce, powdered beverage (orange) and Nigde Bor spring water samples, separately. The resulting solutions were submitted to the procedure given in Section 2.3. The results are given in Table 4 for chili powder, tomato sauce, powdered beverage (orange) and in Table 5 for Nigde Bor spring water. The recovery values for Sudan orange G were in the range of 90–96%. These values show that the method could be applied to the enrichment-separation of Sudan orange G from real samples.

3.9. Applications

The procedure was successfully applied to the separation, enrichment and determination of Sudan orange G in chili powder,

Table 4Addition/recovery tests to Chili powder, tomato sauce and powdered beverage samples ($N = 3$).

Added (μg g ⁻¹)	Chili powder		Tomato sauce		Powdered beverage (orange)	
	Found (μg g ⁻¹)	Recovery (%)	Found (μg g ⁻¹)	Recovery (%)	Found (μg g ⁻¹)	Recovery (%)
0	163.6 ± 4.1 ^a	–	BDL	–	BDL	–
25.0	187.1 ± 4.3	94	22.9 ± 0.3	92	22.5 ± 0.4	90
50.0	209.8 ± 5.5	92	45.1 ± 1.4	90	47.1 ± 1.2	92
75.0	236.3 ± 7.1	96	70.5 ± 2.5	94	66.7 ± 2.5	89

BDL, below the detection limit.

chili sauce and tomato sauce from Turkey. The results for Sudan orange G contents of these samples are given in Table 6.

4. Conclusions

A simple, membrane filtration method was established for the enrichment, separation and determination of Sudan orange G in food and water samples. The effects of matrix components were tolerable. The cellulose acetate membrane could be used eight times. Due to the relatively high preconcentration factors obtained, trace amounts of Sudan orange G at trace level could be accurately determined.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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