



Extended Abstract (Fulltext available in Turkish*)

A Simple fluorimetric method to determine Sudan I dye in spices

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ABSTRACT

Keywords:

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A simple method was developed to determine Sudan I, a banned food dye, in various spices by using its intrinsic fluorescence property. The proposed method was used in the determination of red pepper, sumac and cumin samples to which were added Sudan I dye after being obtained from the local sources. The accuracy of method has been verified by spike and recovery experiments. The recovery values of Sudan I were found in the range of 96.6% - 97.6% for pepper, sumac and cumin. A kind of standard addition method was used to increase the effect of matrix match. Detection limits were 1.0, 0.2 and 0.3 mg/L for red pepper, sumac and cumin, respectively. When compared with the methods in the literature, the proposed method is simple, environmentally friendly and low cost to determine the quantity of Sudan I in spices such as pepper, sumac and cumin.

1. Introduction

Sudan dyes are synthetic azo dyes, used in textile and cosmetic products. Although they are not suitable for being used in foods due to their possible carcinogenic effects, they are still being used as food dyes in order to increase the color intensity of various foodstuffs [1-3]. In the European Union and several other countries, their use in food is prohibited by law [4]. However, traces of these dyes are still present as contaminants in various foodstuffs in many countries.

Sudan I (1-phenylazo-2-naphthol) is the most frequently used dye among Sudan dyes for coloring various spice, especially curry powder and chili powder [5-8]. Many methods to determine Sudan I in spices based on electrochemical measurements [7,9,10], plasmon resonance light scattering (PRLS) [11], surface-enhanced Raman scattering spectroscopy (SERS), [12] HPLC techniques, [13] FTIR, [14] and ELISA [15,16] are reported in the literature. Most of the determination methods of Sudan I dye are based on liquid chromatography [13,17-19]. Although these methods are very sensitive, they are expensive and time-consuming. Generally, they need various extraction procedures including other chemicals and materials to clean up the sample and complicated systems to detect Sudan I [20-27]. Toxic extraction solvents such as acetonitrile, n-hexane and methanol have been used for the sample preparation [13,14]. As a result, the development of new analytical methods that allow simple, rapid, environmental and economic determination of Sudan dyes is still a topic of research. Since Sudan I should be used at a concentration range of about 100 to 1000 mg / kg to obtain effective color in spices [13,14], the development of simple and inexpensive methods for the determination of Sudan I at these concentrations will be enough to detect the dye in spice samples.

Molecular fluorescence spectroscopy allows the development of methods with high sensitivity depending on the fluorescence property of the molecule used. There is a limited number of studies based on fluorescence measurements for detection of Sudan I in spices [28-32]. However, these methods involve the use of a reagent and a material that will interact with the analyte as in most other methods in the literature. Huang et al. reported a fluorescence method with very low detection limit based on the ligand exchange mechanism of Cu(II)-

calcein complex used to determine Sudan I [28]. Chen et al. proposed a method based on the use of polyethylenimine-coated copper nanoparticles [29], while Ling et al. reported the use of polyethylenimine-coated silver nanoparticles as fluorescent probes to determine Sudan I in chili powder [31]. Fang et al. reported the fluorescence quenching method based on the inner filtration effect with a nanomaterial which requires laborious and time-consuming synthesis process [30]. Recently, Di Anibal et al. have proposed a synchronous fluorescence method and multivariate classification analysis for the identification of Sudan I dye in spices [32]. This method of using isopropyl alcohol as an extraction solvent is based on the intrinsic fluorescence property of Sudan I. However, the authors reported that isopropyl alcohol extracts were used in the preparation of samples adulterated to Sudan I. This raises doubt on the validity of the recovery results obtained. Furthermore, the authors did not mention the detection limit and the linear interval [32].

This paper describes a new simple and time-saving method for determination of Sudan I in various spices. The method is based on measuring the intrinsic fluorescence property of the Sudan I dye. A simple and environmentally friendly method was developed, based on the measurement of the fluorescence intensities of the non-toxic ethanolic extracts obtained after extraction of the solid spice samples spiked. The possible matrix effect was removed by a modified standard addition method. Similar standard addition approaches have been used by our research group in the determination of some metal cations by fluorimetric methods [33-36]. A much simpler, cheaper, faster and more environmentally friendly method of determination has been developed compared to the determination method of Sudan I in the literature. The limits of determination of the method are at a level that will enable the detection of red pepper, sumac and cumin powder.

2. Materials and Methods

2.1. Instrumentation

A PTI-QM4 spectrofluorimeter was used to measure fluorescence intensity. The excitation wavelength was 300 nm and the fluorescence emission spectra of Sudan I were recorded in the range of 310-510 nm with a slit width of 1.0 nm.

2.2. Reagents

Ethanol (spectroscopic grade) was purchased from Merck. Sudan I was purchased from Sigma Aldrich. Stock solution of Sudan I (1000

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mg/L) was prepared by dissolving the appropriate amount of the dye in ethanol. Appropriate dilution of the stock solution was carried out to obtain working standard solutions.

2.3. Samples

Red pepper, sumac and cumin samples were purchased from local sources and non-adulterated. To prepare the adulterated samples, the appropriate amount of Sudan I was added to the purchased spice samples and homogenized with a blender. Extraction of the dye with ethanol was applied to both the adulterated and non-adulterated samples.

5.0 g of each sample was shaken at 250 rpm in 100 mL of ethanol for 20 min. After this treatment, the mixture was stirred for 5 min, held in an ultrasonic bath and filtered through a 0.45 μm membrane. The resulting filtrate was used directly in modified standard addition method as sample solution.

2.4. Proposed method for Sudan I determination

The method is based on the fluorescence quenching with the increasing Sudan I concentration. Sudan I content of the samples was determined by using a kind of standard addition method. A similar procedure has already been used for methods based on fluorescence quenching [33-36].

A constant amount of Sudan I and 500 μL of non-adulterated sample solution were added to a series of tubes. Except for the first tube, an aliquot of adulterated sample solution was added to all tubes. Then, increasing amounts of Sudan I was added to the third and the next tubes. The final volumes were completed to 1 mL using ethanol. Fluorescence intensity was measured at the related wavelength for all solutions. From Eq. 1, Sudan I concentration was calculated:

$$C_x = \frac{F_0 - F_1}{m} \quad (1)$$

where C_x is the Sudan I concentration of the sample in the tubes. F_0 and F_1 represent fluorescence intensities of the solution in the first and second tubes, respectively. In Eq. 1, m represents the slope of the standard addition graph. In this procedure, the difference between F_0 and F_1 is proportional to the Sudan I concentration of the sample in the tubes.

3. Results and discussion

Fig. 1 shows the structure of Sudan I dye. As evident from the structure, the dye is expected to act as a fluorescent compound. Several fluorimetric methods based on fluorescence measurements to determine the dye are available in the literature [28-32]. In this study, we intend to use the fluorescence property of the dye. For this purpose, some preliminary studies were carried out.

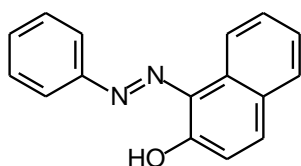


Fig. 1. Structure of Sudan I

A series of Sudan I solutions in ethanol (0.3-50.0 mg/L) were prepared and the fluorescence spectra of the solutions exciting at 300 nm were recorded. As seen from Fig. 2, a regular fluorescence quenching was observed with the increasing Sudan I concentration. A linear concentration range was obtained between 0.3 and 30.0 mg/L from the fluorescence intensities at 330 nm. The linearity continued until 30.0 mg/L, and there was a deviation from Beer's Law after this concentration (Fig. 2 inset). The linear range was used as an external calibration line to determine Sudan I in the adulterated samples. However, the recovery results were not acceptable in the dye determination in samples with the external calibration graph. To

obtain high recovery, a modified standard addition method was used in Sudan I determination. Table I gives the analytical performance data of the method under the optimized conditions.

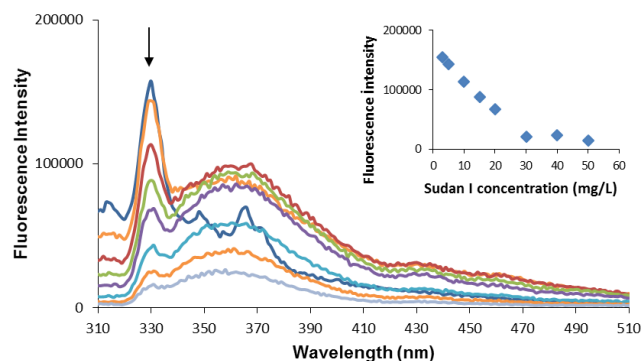


Fig. 2. Change in the emission spectra of Sudan I with increasing the dye concentration. Inset: Change in fluorescence intensity with increasing Sudan I concentration in the range of 0.3 to 50.0 mg/L at 330 nm.

Table 1. Analytical performance data of the presented method for Sudan I determination

	Red pepper	Sumac	Cumin
Excitation wavelength (nm)	300	350	400
Emission wavelength (nm)	330	417	465
Limit of detection (mg/L)	1.0	0.2	0.3
Limit of quantification (mg/L)	3.0	0.5	1.0
Linear range (mg/L)	3.0-10.0	0.5-10.0	1.0-12.0
Constant Sudan I conc. (mg/L)	3.0	6.0	5.0
Non-adulterated sample solution volume (mL)	0.5	0.5	0.5
Total volume (mL)	1.0	1.0	1.0
Solvent	ethanol	ethanol	ethanol
Incubation time	no time	no time	no time
Correlation coefficient (R^2)	0.9975	0.9964	0.9956
Intra-day precision (RSD%, N=3)	3.1	4.3	2.2
Inter-day precision (RSD%, N=3)	3.7	4.7	2.4

3.1. Sample preparation and extraction

Sample preparation stage is a critical stage in the determination of Sudan dyes due to the need of an effective extraction of the dye. For this, various extraction techniques have been used. Solid-liquid extraction techniques with organic solvent are widely used to extract Sudan I from spices [13,16,18,29,31,32]. The recovery values depend on both the solvent and the matrix in these studies. Acetonitrile, acetone, n-hexane, methanol, ethanol and isopropyl alcohol are the most common solvents for this in the literature. In the present study, ethanol is preferred as solvent because of its cheapness, harmlessness and high ability to solve Sudan I.

At this point, it should be noted that the spiking procedure also affects the recovery results. Generally, Sudan I has been added to original spice samples to prepare spiked samples in the literature. However, there are also some studies in which Sudan I are added to the sample extracts with organic solvent to prepare the spiked samples [31-32]. The recovery results obtained by this type of spiking procedure could be different from that of spiking to the original spice sample. In the present study, both spiking procedures were carried out. It was clear that very high recovery values were obtained when Sudan I was added to the sample extracts. However, this procedure is not suitable to monitor Sudan I in real adulterated spice samples. For meaningful recovery results, Sudan I was added to the original spice samples in the spiking process.

3.2. Analytical performance

The critical parameter in the modified standard addition method is to optimize the constant Sudan I concentration. The constant Sudan I concentration was optimized by changing Sudan I concentration from

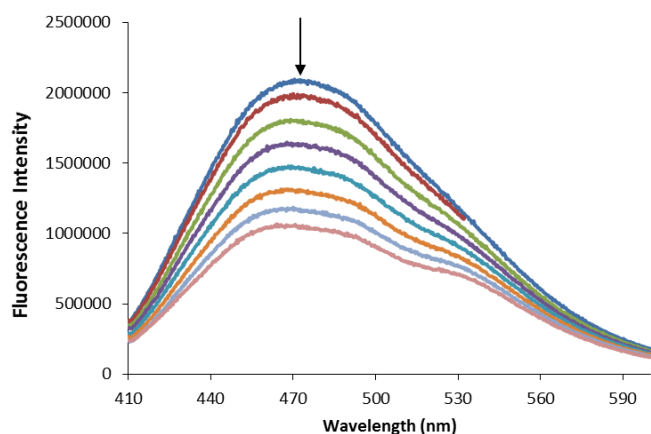


Fig. 3. Change in the fluorescence spectra of the solution used in the modified standard addition method for cumin. Sudan I concentration: 1.0 mg/L.

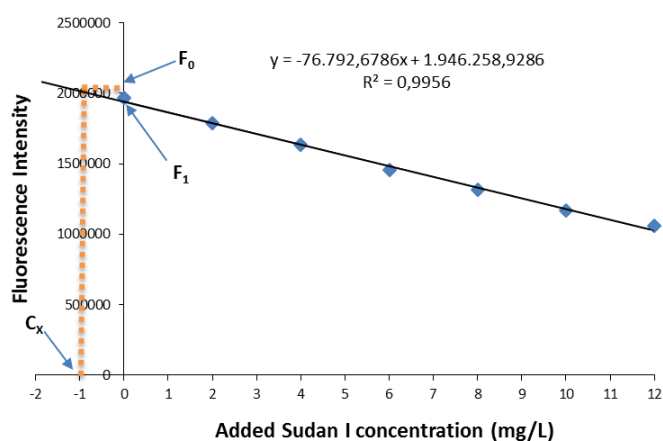


Fig. 4. Modified standard addition graph used in Sudan I determination for cumin. Sudan I concentration: 1.0 mg/L.

Table 2. Determination of Sudan I in various spices (N = 3)

Sample	Added (mg/L)	Found±BSS% (mg/L)	% Recovery
Red pepper	3.0	2.9 ± 3.1	97.6
	4.0	-	96.5
Sumac	0.5	0.5 ± 4.2	96.6
	0.6	-	97.4
	2.0	-	96.3
Cumin	1.0	1.0 ± 1.9	96.8
	2.0	-	97.5
	4.0	-	96.5

--: Not determined.

0.5 to 8.0 mg/L for each sample matrix. The optimum constant Sudan I concentrations were 3.0, 6.0 and 5.0 mg/L for red pepper, sumac and cumin, respectively (Table 1). The relative errors below 5% in the recovery experiments were considered in the determination of the optimum constant Sudan I concentration. 0.5 mL of the non-adulterated sample solution was used to provide matrix matching in the modified standard addition procedure for all measurements. The LOD value was calculated to be $3s/m$ and LOQ value was 3 times the LOD. s is standard deviation of fluorescence intensity of 11 blank solutions, and m is slope of calibration equation.

The fluorescence spectra of solutions prepared for the determination of Sudan I in the cumin sample are shown in Fig. 3, and the corresponding standard addition graph is shown in Fig. 4. As can be seen from Fig. 4, the concentration of Sudan I in a sample can also be found by extrapolation.

The solutions prepared for each sample matrix are schematically shown in SI. The change of fluorescence spectra and the calibration graphs for the determinations made on red pepper and sumac samples are given in Figs. S3-S4 and Figs. S6-S7 in SI.

The accuracy of the method was verified by analyzing spice samples spiked at two (red pepper) and three (sumac and cumin) Sudan I concentration levels. The recovery values were quite satisfactory for all samples (Table 2). The results showed that the method can be applied for the determination of banned dye Sudan I in spice samples.

Table 3 summarizes some of the methods recommended for determination of Sudan I in various spices in the literature. The methods summarized in Table 3 are mostly fluorimetric methods and allow comparison with the method proposed in this study. The detection limits of the known methods in the literature are lower than the recommended method, but require laborious pre-treatment or extraction steps prior to determination. Moreover, the methods also need the use of some chemical reagents or the preparation and use of

Table 3. Analytical and operational parameters of the presented method and previously reported methods in the literature

Method	Sample	Reagent	Sample preparation procedure	Linear range (mg/L)	LOD (mg/L)	Ref.
SF	Red peper, sumac, cumin	-	Extraction for 20 min with ethanol after ultrasonication for 5 min	0.5-12	0.3-1.0	Presented method
SF	Red and smoked paprika	-	Shaking for 15 min with isopropyl alcohol	-	-	32
SF	Chili powder	Cu(II)-calcein complex	Pretreatment according to the method of National Standard of the People's Republic of China (2005)	0.0028-0.51	0.000052	28
SF	Chili powder	Polyethyleneimine-capped silver nanoclusters	Extraction with ethanol, vortex for 5 min, sonication for 30 min, waiting at ambient temperature for 10 min, centrifugation of supernatant for 3 min, using PEI-AgNCs	0.0992-6.2	0.0027	29
SF	Hot Chili powder	Polyethyleneimine-coated copper nanoclusters	Pretreatment of the sample by the method of National Standard of the People's Republic of China (2005)	0.0248-7.44	0.0161	31
HPLC-UV	Chili powder	-	Cloud point extraction using Triton X-100, dilution of the surfactant-rich phase with acetone-water mixture before injection in HPLC	-	-	24
ELISA	Spice mix, curry powder, Chili powder	Carboxy-Sudan I conjugated to HRP	Shaking for 15 min with acetonitrile after mixing 5 s, dilution with methanol, and a gel permeation clean-up procedure	-	-	16

nanomaterials. For this reason, they are time consuming and expensive methods. The presented method needs only standard Sudan I and the simple extraction of the dye before the determination step.

4. Conclusion

The method is based on fluorescence quenching of Sudan I in ethanol with increasing dye concentration. The proposed method is effective in various spices such as red pepper, sumac and cumin. One of its many advantages is that a green and simple extraction process is used before the determination stage. The usage of a reagent and sample treatment stage before measurement are both not needed in the proposed method. The modified standard addition method with matrix matching handles the possible matrix effect. It does not require an incubation period to obtain a stable fluorescence response before measurement. Consequently, these advantages make the proposed method time-saving, simple and economic compared to other methods in the literature.

SUPPORTING INFORMATION

The supplementary material associated with this article is available on-line.

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