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Solid-phase extraction and determination of erythrosine in water using aluminum oxide column

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ABSTRACT

A novel use of aluminum oxide for Erythrosine E127 preconcentration from water is reported. E127 is effectively adsorbed by aluminum oxide column and eluted using small amount of tetrahydrofuran. Under the studied extraction conditions, 100 µg/L of E127 was quantified with high accuracy (98%) and precision (%RSD 8). A high enrichment factor (113) is obtained by the proposed extraction procedure which is necessary for trace analysis. Using principal component analysis, the %recovery of E127 is correlated to the experimental factors as: %recovery = 0.09 (Samp Vol) + 0.19 (Mass) + 0.59 (Eluent Vol) – 0.17 (pH). The PCA revealed that eluent volume, aluminum oxide mass, and sample volume are positively correlated with %recovery while pH is negatively correlated with %recovery. The most significant factor on E127 preconcentration from water is the eluent volume with a coefficient value of 0.59. The extraction procedure was effective for determination of E127 in tap water at 100 µg/L. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Erythrosine (E127);
Aluminum oxide;
SPE;
Principal component
analysis.

INTRODUCTION

Erythrosine (E127) is a common food colorant. When excessively consumed, it can cause sensitivity to light, affecting thyroid hormone levels and lead to hyperthyroidism in some cases^[1]. The maximum allowed level of erythrosine should be less than 0.2 mg/g in some foodstuffs^[2]. Monitoring and determination of E127 in real water samples is essential due to its potential toxicity and pathogenicity^[2]. Various analytical methods such as spectrophotometry^[3], capillary

electrophoreses^[4] liquid chromatography/UV detection^[5], and micellar electro kinetic capillary chromatography/UV and MS detection^[6] are often used for dyes quantification in water. Unfortunately, dyes are often present at very low levels (usually in µg or ng levels) in real water streams which retard their direct quantification by most instruments^[7]. Accordingly, a preconcentration step is necessary prior to chemical analysis in order to get a quantifiable amount of the dye. Moreover, reducing sample interferences is necessary to improve the sensitivity of chemical analysis. In

order to overcome these problems, preconcentration and separation procedures such as solid phase extraction and liquid-liquid extraction are used^[8]. Solid phase extraction SPE is recommended by many researchers due to its many technical advantages over other procedures^[3]. Very high preconcentration factors are easily obtained using SPE compare to liquid-liquid extraction^[8]. Many natural and synthetic extractants were tested for dyes preconcentration including polystyrene-divinylbenzene^[7], C₁₈ column^[5], imprinted polymers^[9], diatomite/zeolite^[10], iron oxides^[11], surfactant-coated alumina^[3].

Very limited studies have considered adsorption/preconcentration of E127 in real water. At the best of the authors' knowledge, adsorption/preconcentration of E127 by aluminum oxide do not investigated in the literature. Activated carbon and de-oiled mustard showed high adsorption values for E127, 161 and 147 mol/g, respectively^[12]. However, the earlier adsorbents are not tested as solid-phase extractant for E127.

In this work, the application of aluminum oxide for extraction and preconcentration of E127 is studied. The effect of aluminum oxide (extractant) mass, pH, eluent volume, sample volume on dye preconcentration is studied and optimized. Analysis of trace levels ($\mu\text{g/L}$) of E127 in tap water using aluminum oxide as SPE is studied. Using principal component analysis, the dominant experimental factors on E127 preconcentration are assessed.

EXPERIMENTAL

Chemicals and solvents

Erythrosine was purchased from Sigma[®] Company (purity 99.9%). The chemical structure of Erythrosine is given in Figure 1.

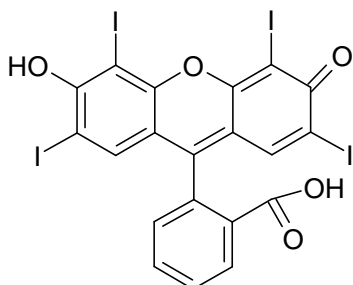


Figure 1 : Chemical structure of erythrosine (E127).

A 250 mg/L standard solution of E127 was prepared by dissolving appropriate amount of dye in distilled water, diluted to one liter, and the final pH was adjusted to 7.0 using 0.01 M HCL. Diluted solutions were prepared from the stock one. All solutions were kept in a dark and cold place. The other chemicals and solvents were of analytical or HPLC grades and obtained from TEDIA (Ohio, USA). Aluminum oxide Al₂O₃ (in the basic form) was obtained from BDH Company.

Determination of E127 by vis-spectroscopy

E127 was quantified in tetrahydrofuran THF (the eluent) using UV/Vis-spectroscopy (Cary 50 UV-Vis spectrophotometer, Varian, USA) at λ_{max} 528 nm. Beer's law is obeyed over the concentration range 1.94-10.0 mg/L with a high degree of correlation, $r^2 = 0.9982$. The proposed method is fairly sensitive with 0.58 and 1.94 mg/L as detection limit ($3\sigma_{\text{blank}}$), and limit of quantification ($10\sigma_{\text{blank}}$), respectively. Figure 2 shows the spectrum of erythrosine recorded at 20 °C and pH 7.0.

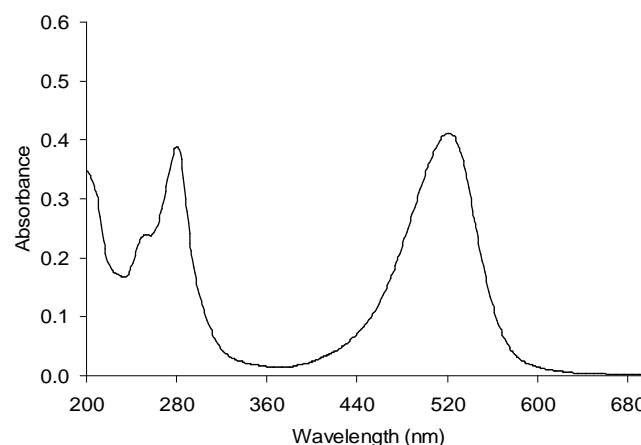


Figure 2 : Absorption spectrum of 10.0 mg/L dye solution at pH 7 ($\lambda_{\text{max}} = 528 \text{ nm}$).

E127 Preconcentration from natural waters

The preconcentration of E127 was carried out using a glass column of 150 mm length and 10 mm internal diameter. The column was packed with aluminium oxide and the dye solution containing 100 $\mu\text{g/L}$ was passed through the column at a flow rate of 7.0 mL/min. The adsorbed dye was eluted with THF and collected in a small polyethylene bottle. The concentration of E127 was measured by the spectrophotometer using a pre-plotted calibration graph. Effect of sample

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volume, extractant mass, pH, and eluent volume on E127 preconcentration was studied.

Principal component analysis

Four factors that affect E127 preconcentration were studied. The dominant factor (s) among the studied factors on E127 extraction/preconcentration is/are assessed using principal component analysis PCA. PCA is a powerful statistical method that used for factor analysis, clustering of objects and also for modeling purposes^[13]. PCA was carried out as outlined in the literature using Matlab[®] software^[13].

RESULTS AND DISCUSSION

Effect of experimental factors on E 127 recovery

The effect of varying extractant mass, pH, dye level, eluent volume, and sample volume on E 127 recovery/preconcentration was studied at 25 °C and flow rate of 7 ml/min. The results are summarized in Table (1). In most extractions, the initial level of E127 was 100 µg/L and at this level the accurate determination of E127 is not possible where the limit of quantification is 1.94 µg/L (see section 2.2).

As can be noted in TABLE 1, the %recovery of E127 at 100 µg was increased from 43 to 75% by increasing the mass from 1000 to 4000 mg. This behavior is predicted as more active sites will be available for dye extraction at higher masses. The optimum aluminum oxide mass was kept at 4000 mg in the next extractions. Similar results were reported in the literature^[14-15]. The enrichment factor EF of E127 is estimated as follows^[16].

$$\text{Enrichment Factor} = (V_i/V_f) \times \text{Recovery} \quad (1)$$

where V_i and V_f are the initial sample volume (volume before preconcentration) and the final volume obtained after preconcentration. The results indicated that a high EF is obtained as the mass of the extractant increased. The volume of the elution reagent should be as small as possible to get a better detection limit of the method^[14-16]. Four solvents were tested dye elution: ethanol, acetic acid, 0.1 M HCl, and tetrahydrofuran THF. Among the tested agents, THF was effective for eluting E127 and TABLE 1 indicated that as the volume of THF increased better preconcentration recovery is obtained. Similar results were ob-

TABLE 1 : Preconcentration of E127 at different experimental factors.

Weight (mg) ¹	C _{initial} (µg L ⁻¹)	C _{detect} (mg L ⁻¹)	Recovery %	EF
1000	100	4.4	43.5	44
2000	100	6.0	60.4	60
3000	100	6.9	69.2	69
4000	100	7.4	74.4	74
THF (mL)²				
5.0	100	6.3	31.5	63
10.0	100	7.3	73.3	73
15.0	100	6.1	91.5	61
20.0	100	4.9	98.0	49
pH³				
3	100	7.3	72.6	73
6	100	7.0	70.4	70
7	100	7.3	73.8	71
8	100	4.5	45.2	45
10	100	3.9	39.3	39
Sample volume(mL)⁴				
250	100	1.5	60.1	15
500	100	3.3	66.4	33
1000	100	7.1	71.3	71
1500	100	11.3	75.3	113

1. Dye content 100 µg/L, 25 °C, flow rate 7ml/min, THF volume 10 mL, sample volume 1000 ml, pH 7. (Average of three trials. RSD < 8.5%)

2. Dye content 100 µg/L, flow rate 7ml/min, 25 °C, pH 7, sample volume 1000 mL, and Al₂O₃ mass 4000 mg. (average of three trials. RSD < 8%).

3. Dye content 100 µg/L, flow rate 7ml/min, Al₂O₃ mass 4000 mg, sample volume 1000 mL, THF volume 10 mL, and 25 °C. (average of three trials. RSD < 10%).

4. Dye content 100 µg/L, flow rate 7ml/min, Al₂O₃ mass 4000 mg, pH 7, 25 °C, and THF 10 mL. (average of three trials. RSD < 6%).

served when stripping heavy metals using different volumes of 1.0 M HNO₃^[15].

Dye recovery has been gradually increased with eluent volume and remains unchanged after 15 mL. As indicated in TABLE 1, the maximum EF was 73 achieved at 10 mL eluent volume, therefore, eluent volume was maintained at 10 mL. As shown in TABLE 1, the %recovery of E127 was 72.6% at acidic pH and reduced to 39% at basic conditions. The EF values were 73 at pH 3 and 39 at pH 10 indicating the poor extraction performance at basic conditions. The variations in E127 extraction with solution pH is explained ac-

ording to following mechanism. At pH 3, the surface of aluminum oxide is positively charged because solution pH is less than pH_{zpc} which is equal to 7.0^[17] and this would increase dye uptake via interaction with π -electronic system in the dye molecule. However, the large reduction at basic solution is attributed to the electrostatic repulsion between negatively charged aluminum oxide (due to adsorption of OH^- ions on the surface) and the deprotonated dye molecule. Sample volume has a high influence on E127 preconcentration. As can be seen in TABLE 1, the extractant showed a large enrichment capacity of E127 where the highest EF was 113 and obtained at 1500 mL. Furthermore, good %recoveries ($> 70\%$) were obtained at sample volumes more than 1000 mL. Similar observations were reported using microemulsion-modified-zeolite for reactive dyes preconcentration^[18]. In order to reduce analysis time and obtain a high EF, 1000 mL was selected as the optimum sample volume. In fact, the high EF reflects the excellent extraction efficiency of aluminum oxide for E127. In a related study, high EF values (90-97) were reported for preconcentration of cationic dyes using natural diatomite^[10].

Determination of E127 at 50 $\mu\text{g/L}$ was studied under the following extraction conditions: Temperature 25 °C, flow rate 7ml/min, THF volume 10 mL, Al_2O_3 mass 4000 g, sample volume 1000 mL, and pH 7. Five identical determinations were carried out. In fact, direct determination of E127 is not possible at such trace level (50 $\mu\text{g/L}$) where the limit of quantification is 1.94 mg/L. The results indicated that the E127 is determined at 50 $\mu\text{g/L}$ with a fair accuracy (71.2%) and precision (%RSD 4.7-12.6).

Preconcentration of E127 from tap water: Effect of sample complexity

This study was undertaken in order to evaluate the potential application of aluminum oxide for selective preconcentration of E127 that present in tap water. The preconcentration of E127 in tap water was studied at 100 $\mu\text{g/L}$. The other extraction conditions were maintained at: temperatures 25 °C, flow rate 7ml/min, 10 mL THF, oxide mass 4000 mg, pH 7, sample volume 250, 500 and 1000 mL.

The results were given in TABLE 2.

TABLE 2 : Preconcentration of E 127 at 100 $\mu\text{g/L}$ in tap water* (average of three trials, RSD < 18%).

Volume mL	C_{initial} ($\mu\text{g L}^{-1}$)	C_{detect} (mg L^{-1})	Recovery %	EF
250	100	1.4	56.3	14
500	100	3.3	67.4	33
1000	100	7.2	72.8	72

* Analysis on tap water revealed the presence of: Cl^- 500 ppm, SO_4^{2-} 18ppm, and total hardness (as $CaCO_3$ and $MgCO_3$) 600 ppm.

It should be mentioned that blank samples of tap water were subjected to the extraction procedure to check out the presence of E127 or other interfering compounds that would absorb at 548 nm. The results indicated the absence of E127 in tap water and also insignificant interference of other compounds on spectrophotometric analysis. At 1000 mL of pure water and pH 3, the % recovery and EF were 72.6% and 73 (See TABLE 1) and similar results were observed in TABLE 2. The dissolved inorganic species in tap water do not seriously interfere with E127 adsorption by aluminum oxide. In a related study, an imprinted polymer was prepared for selective extraction of cibacron reactive red dye from water^[9]. The earlier extractant was found effective for red dye extraction from pure water with a preconcentration factor of 100. However, the preconcentration factor was reduced to 89 in tap water and this reduction is attributed to the competition between water interferences and the red dye^[9].

Principal component analysis of preconcentration results

By conducting 17 extraction experiments, the effect of sample volume, extractant mass, pH, and eluent volume on E127 extraction/preconcentration was assessed. Accordingly, a matrix of dimension 17×4 and a response vector (%recovery values) of dimension 17×1 were obtained. The earlier data were collected from TABLE 1 and subjected to PCA for assessing the influence of each factor on E127 preconcentration.

Initially, the data were mean-centered prior to PCA analysis and the following empirical equation was obtained:

$$\% \text{recovery} = 0.09 (\text{Samp Vol}) + 0.19 (\text{Mass}) + 0.59 (\text{Eluent Vol}) - 0.17 (\text{pH}) \quad (2)$$

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Student's *t*-test was used as a statistical indicator to assess the significance of each factor in the earlier relation provided that more experiments (17 experiments) were performed than number of factors (four factors). The significance *t*-test was carried out as following^[13]: a) the square covariance matrix was calculated and the variances (*v*) (the diagonal values of covariance) were obtained, b) S_E , the error sum of squares, which calculated from the experimental & true values and the predicted values, c) determination of mean error sum of squares (*s*) by dividing S_E by number of degrees of freedom which equals to $N-P$, where N is number of experiments and P is the number of factors, and d) estimation of *t*-value, $t = \frac{b}{(sv)^{1/2}}$ and the higher

this ratio, the more significant is the factor at the desired confidence level. The obtained *v* and *t* values were summarized in TABLE 3 for both experiments.

TABLE 3 : Significance *t*-test for the importance of experimental factors

	Coefficient	<i>v</i>	<i>t</i>
Samp Vol	0.09	5171	0.001
Mass	0.19	120	0.015
Eluent Vol	0.59	85	0.514
pH	-0.17	60	0.148

$S_E = 17.2$, $s = 1.32$, and $N-P = 13$.

The tabulated *t* value at 17 degree of freedom is 2.08 at 95% confidence level. For all factors, the calculated *t* values were much less than t_{table} . Accordingly, the studied factors are all significant for E127 preconcentration from water, however, with different correlation. As shown in Equation 2, oxide mass, eluent volume, and sample were positively correlated with %recovery, while, pH was negatively correlated with %recovery. Moreover, THF volume was the dominant factor among the studied factors because it has the maximum coefficient (0.49) and sample volume has a small effect on E127 preconcentration with a coefficient of 0.09. Based on that, the best extraction conditions will be: 4000 mg oxide, 20 mL THF, 1500 mL sample volume, and pH 3. The prediction power of equations 2 was further tested by re-estimating % recovery and the relative error of prediction REP% was also calculated. Figure 3 shows the plots between experimental and predicted values of %

recovery with the lower and upper error margins calculated at 95% confidence level.

As indicated in Figure 2, the prediction power of equations 2 is acceptable with a good correlation coefficient of 0.7712. The obtained REP%

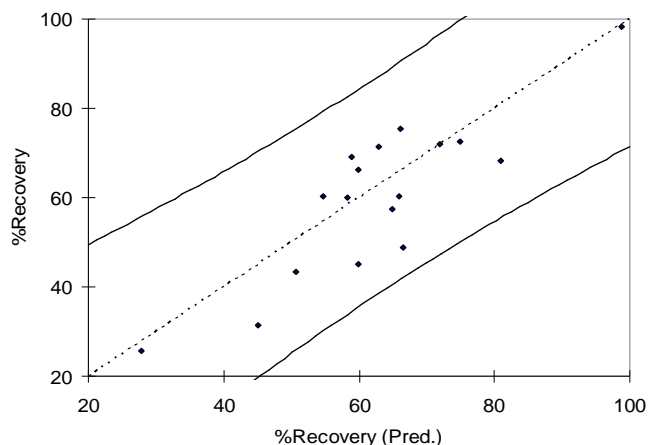


Figure 3 : Prediction of %Recovery as obtained from equation 2.

value was 8.3% which also reflects the high credibility of the derived empirical equation.

CONCLUSIONS

Using aluminum oxide column, the toxic food dye E127 is determined in water at trace level, 50 µg/L. A high enrichment factor is achieved in this work (113) which enables detection of E127 at trace levels. The performance of aluminum oxide for E127 preconcentration was not affected when extraction is carried out in tap water. Principal component analysis revealed that eluent volume, oxide mass and sample volume are positively correlated with %recovery and pH is negatively correlated with %recovery. PCA revealed that the best extraction conditions would be 4000 mg oxide, 20 mL THF, 1500 mL sample volume, and pH 3.

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