Quantitative Analysis of Iron in Eye Shadow Samples by Vortex-Assisted Dispersive Liquid-Liquid Microextraction with Deep Eutectic Solvent based and Spectrophotometry

Mrunmayi C[1], Dilip Y[2], Suhas J[3], Himani M[4]
[1,2,3,4] Department of Chemistry, Sonopant Dandekar College, 4014074, Maharashtra, India

http://doi.org/10.64643/IJIRTV12I5-185677-459

***Abstract*—Eye shadow is a prominent example of cosmetics that include heavy metals, with iron present in greater concentrations than other metals. This work developed an environmentally sustainable analytical method for quantifying iron in eyeshadow samples using Vortex-Assisted Dispersive Liquid-Liquid Microextraction (VA-DLLME) with deep eutectic solvent (DES) as the extractant, followed by spectrophotometric analysis. DPC, or 1,5-Diphenylcarbazide, acted as a complexing agent that forms a complex with Fe (III) at pH 5. The Fe-DPC complex was vortexed for 30 seconds at 2800 rpm to completely extract the complex into a non-aqueous phase. A variety of parameters was carefully analysed to improve the extraction efficiency of iron. Under typical conditions, the calibration curve demonstrated linearity between 7.0 µg/L and 70 µg/L, with a limit of quantification (LOQ) of 5.63 µg/L and a limit of detection (LOD) of 1.86 µg/L. The enrichment factor was established at 40, and the relative standard deviation was calculated to be 2.11%. The approach was evaluated using a certified Fe(III) solution and successfully employed to determine iron content in eye shadows.**

***Index Terms*—Eye Shadow, Iron, Deep Eutectic Solvent, DLLME, 1,5-Diphenylcarbazide**

I. INTRODUCTION

In today's modernised era, people are highly conscious of their appearances and show a strong interest in enhancing their looks. Cosmetics encompass a diverse range of products such as compact powders, lipsticks, kajal, eyeshadows, toothpaste, shampoos, conditioners, mascaras, nail polishes, and facial and eye makeup, which have become essential components of daily routines[1]. Brockhaus defines cosmetics, as per the German Food and Commodities Act of 08/15/1974, as substances or preparations intended primarily for external application on the human body or within the oral cavity. Their purposes include cleaning, personal hygiene, altering appearances or body odours, and imparting fragrance[2]. The colour of cosmetics results from the incorporation of colouring agents[3]. Furthermore, the colourants are classified according to their structure, colour, solubility, and application. These substances are classified as dyes and pigments according to their solubility. Dyes are synthetic organic compounds that are soluble in oil, while pigments are primarily insoluble compounds utilised in eye shadow[4]. The primary metals found in eye shadow include iron, chromium, aluminium, cadmium, nickel, copper, cobalt, manganese, and zinc, etc[5]. The average concentration of these metals in the facial cosmetics varied as follows: 0.23–2.8% Fe, 0.091–0.44% Cr, 0.031–0.084% Cd, 0.12–2.4% Ni, 0.016–0.8% Cu, 0.079–0.17% Co, 0.12–2.3% Mn, and 0.18–3.2% Zn[6]. According to the World Health Organisation (WHO), the maximum amount of iron that can be included in cosmetics is 0.3 ppm[7].

Iron is a fundamental ingredient found in eye shadows[8]. Iron oxides, which display colours ranging from black and brown to red and yellow, are widely employed as pigments in many cosmetics, especially in eye shadows[9]. Cosmetics can trigger two types of dermatitis: allergic contact dermatitis and irritating contact dermatitis. Excessive iron consumption can be harmful, leading to symptoms such as throat and nasal discomfort, nausea, vomiting, and even hemochromatosis, a condition characterised by skin pigmentation[10]. Despite being applied directly to the skin, the probability of direct absorption of pigments and other hazardous substances is very minimal. These elements can still enter the bloodstream, even though they may prevent eyelid eczema[11]. Therefore, reliable, precise and accurate analytical methods are essential for measuring trace levels of iron in eyeshadow samples [12.]

Traditional solvent extraction methods for sample preconcentration are tedious and time-consuming and require substantial quantities of organic solvent for extraction[13]. Recent microextraction methodologies, including Cloud Point Extraction (CPE)[14], Liquid-Phase Microextraction (LPME)[15], Homogeneous Liquid-Liquid Extraction (HLLE)[16], Solid-Phase Microextraction (SPME)[17], Single-Drop Microextraction (SDME)[18], and Dispersive Liquid-Liquid Microextraction (DLLME)[19,] have been developed to overcome the limitations associated with conventional techniques.

DLLME, a simple microextraction technique, was first developed by M. Razaee et al. in 2006[20]. This technique involves the forceful injection of extracting and dispersive solvents into the liquid sample, resulting in the creation of a cloudy solution. Once the sediment phase has been separated by centrifugation, it is collected from the bottom of the test tube and subjected to analytical procedures. The most commonly used analytical techniques for the estimation of metals are Flame Atomic Absorption Spectrometry (FAAS)[21], Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[22], Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[23], Electrothermal Atomic Absorption Spectrometry (ETAAS)[24], Graphite Furnace Atomic Absorption Spectrometry (GFAAS)[25], Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES)[26],Atomic Absorption Spectrophotometry (AAS)[27] and, UV-visible spectrophotometry[28]. DLLME methods have significant advantages, including high recovery rates, high enrichment factors, simplicity, cost-effectiveness, and rapidity. Further enhancements in DLLME included dispersion solvent-free physical techniques, including Ultrasound-Assisted (UA-DLLME)[29] and Vortex-Assisted (VA-DLLME)[30]procedures. DLLME methods were extensively utilised in the analysis of cosmetic items, including parabens in aqueous cosmetics[31], mercury in liquid cosmetic samples[32], lead in lipsticks and hair colours[33], and nickel in cosmetic samples[34].

The utilisation of deep eutectic solvents as the extraction medium in dispersive liquid-liquid microextraction is referred to as DES-DLLME. DES is synthesised by combining a hydrogen bond donor with a hydrogen bond acceptor molecule, in either a binary or ternary combination[35]. DES is used as an extracting solvent in this work because of its ease of synthesis, thermal stability, low toxicity, and cost-effectiveness[36].

To our best knowledge, there are no reports on applying the VA- DLLME method for determining Iron in eye shadows. This study aims to develop a more significant method to determine the trace amount of Fe(III) ion in the eye shadow by using a green and inexpensive deep eutectic solvent-based vortex-assisted dispersive liquid-liquid microextraction coupled with a UV-Visible spectrophotometer.

II. MATERIALS AND METHODS

2.1. Materials:

The Iron standard solution 1000 mg/L was obtained from Loba chemie, India and was diluted with appropriate amount of double-distilled water for the future analysis. Ferric sulphate, 1,5-diphenylcarbazide (DPC), sodium acetate, and choline chloride were acquired from Sigma-Aldrich, Mumbai, India. Eugenol was obtained from Loba Chemie Mumbai, India. Deep eutectic solvents were synthesised by mixing eugenol and choline chloride in different molar ratios in a 150 mL beaker. Samples of eye shadow were obtained from the local market in Boisar, India.

2.2Instruments:

The UV-visible spectrophotometer (Shimadzu Analytical, India) and quartz cell were employed to analyse the various characteristics of the iron metal complex. A vortex apparatus manufactured by Remi, India, designed for the purpose of vortex agitation. A centrifuge (Remi, India) was utilised to enhance phase sedimentation. A pH meter manufactured by Thermo Scientific, India, was utilised to determine the pH level of the solution.

2.3. Extraction Procedure:

In a 50 mL flask, 200 µL of 2% chelating reagent (1,5-diphenylcarbazide) at pH 5 was employed to complex 10 mL of an aqueous solution containing 50 µg/L Fe(III) ions. A 250 µL extractant (DES) was rapidly injected into the sample with a syringe to extract the Fe-DPC complex.After injecting, the reaction mixture was vortexed for 30 seconds at 2800 rpm to form a homogenized mixture and dispersion in the solution. This solution was centrifuged for 0.5 minutes at 3000 rpm to settle the complex. After collecting the enriched phase it was, diluted with 1mL ethanol, and analyzed for UV-Visible spectrophotometric measurements at

510nm *against* reagent blank. Ethanol is used solely for diluting the sediment phase, allowing for the convenient determination of the complex's color in a quartz cell

2.4. Sample preparation method:

The developed procedure was based on four different eye makeup samples acquired from a local retailer. 4.0 g of each eye makeup sample was placed in a clean, dry beaker and mixed with 20 mL of a 1:9 ethanol-water solution. The solution was then maintained in a water bath for 15 minutes, cooled and subsequently centrifuged for 5 minutes. Solid sediment phase was discarded and supernatant liquid diluted with appropriate amount of double distilled water. Aliquots of this mixture were used for further analysis.

III. RESULT AND DISCUSSION

The developed method was fast, efficient, and effective but required further optimization of specific factors for efficiency. The optimization parameters, including pH, concentration, and volume of chelating reagent, vortex time, centrifugation parameter, solvent selection and volume, salt addition, and interference of foreign ions, have been discussed in detail. Enrichment factor and extraction recovery are two significant parameters used to evaluate the developed method[37.] The enrichment factor (EF) is the ratio of the analyte concentration in DES to its initial concentration of analyte in the sample. These two variables are calculated by using equations (1) and (2), respectively

$$\% \text{ Recovery} = \frac{W_{des}}{W_O} \times 100 \quad \ldots\ldots\ldots (1)$$

W_{des} - Volume of sample

W_o - Volume of sediment

$$\text{EF} = \frac{C_{des}}{C_O} \times 100 \quad \ldots\ldots.. (2)$$

V_{sample} – Analyte concentration in DES

$V_{sediment}$ – The Initial concentration of analyte in the sample solution

3.1 Characterization of the deep eutectic solvent:

The structural characteristics of the produced DESs were studied using FTIR [Fig. 1]. Choline chloride and eugenol formed an intermolecular hydrogen bond, which led to the synthesis of DES. –OH group in Eugenol shows characteristic IR pick at 3523cm^{-1}. The IR spectra of produced DES no longer show the bandwidth at 3523 cm^{-1} associated with the -OH group in Eugenol. The effective formation of DESs may be concluded from these characterisations.

3.2 Study of the Absorption spectra:

In this study, a UV-visible spectrophotometer was employed to determine various parameters. The iron complex was analysed using the spectrophotometer to obtain the absorption curve. The maximum absorption wavelength (λ max) obtained was 510 nm against the reagent blank [Fig. 2].

3.3 Effect of pH:

The pH of the sample solution plays a crucial role, as it significantly affects the formation of the metal-ligand complex and the subsequent extraction of the formed complex. The effect of the pH was examined between 1.0 and 10.0. Increasing the pH enhances the extraction of the complex up to pH 5.0, after which the extraction decreases [Fig. 3]. Therefore, a pH of 5.0 was chosen for further work.

3.4 Concentration of chelating agent:

The effect of reagent concentration, in relation to the ligand/metal ratio, on the absorption of the complex was studied by varying the concentration and volume of 1,5-diphenylcarbazide (DPC). Different concentrations of the DPC, ranging from 0.5% to 3.0%, were prepared and analysed. The extraction of analytes increases up to 2% and then remains steady in subsequent readings, indicating that 2% reagent is sufficient to form the complex. Different volumes of 2% reagent from 50 µL to 300 µL were added to the metal-complex solution. Maximum extraction was observed at 200µL of reagent [Fig. 4]. Thus, 200 µL of a 2% chelating agent shows maximum extraction and this volume was selected for further studies.

3.5 Effect of Vortex time:

The amount of analyte extracted is influenced by the rate of its mass transfer from the sample solution to the extraction phase. Therefore, determining the optimal agitation time for dispersion is crucial to ensure maximum extraction of the analyte from the aqueous phase into the organic phase. Vortex agitation was performed in a period of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 min. As the vortex time increases, the extraction efficiency improves and eventually stabilizes. Maximum extraction was observed at 0.5 minutes at 2800 rpm [Fig. 5]. Therefore, 0.5 minutes was selected as the vortex time for the experiment. This method requires minimal agitation time.

3.6 Effect of centrifugation time:

The influence of centrifugation time on the extraction of Fe (III) complex was investigated. The centrifugation time was varied between 0.2 and 1.4 minutes [Fig. 6]. The absorbance increased gradually with time, eventually stabilising. Based on this, a centrifugation time of 1.0 minute at 3000 rpm was chosen for further studies.

3.7 Selection of DES and volume:

In the proposed method, the prepared DES should meet the general characteristics such as low solubility in the aqueous phase, high extraction efficiency and low toxicity, and it should form a complex with the selected cations. In the present work, five different DES were prepared using eugenol and choline chloride in molar ratios of 2:1, 1:2, 3:2, 1:3, and 2:3. Among these, the DES with a molar ratio of 2:1 exhibited maximum extraction of the complex. The volume of DES also plays an important role in the extraction process. To optimise this, different volumes of the 2:1 DES, ranging from 50 µL to 300 µL, were tested. A volume of 250 µL demonstrated maximum extraction efficiency and was therefore selected for further studies [Fig. 7].

3.8. Effect of salt addition:

Adding salt in the DLLME procedure enhances extraction efficiency due to the salting-out effect, which reduces the analyte's solubility in the aqueous phase and promotes its transfer to the organic phase. The impact of ionic strength on DES-DLLME was studied using NaCl solutions at concentrations of 2.5%, 5.0% and 10%, while keeping other experimental conditions constant. However, this range of NaCl concentrations showed no significant effect on ionic strength or the extraction process, indicating that salt addition does not influence the efficiency of this method.

3.9 Interferences:

As DPC is a versatile complexing agent to form complexes with other metal ions, thus interferences from metal ions in the eyeshadow sample may occur frequently. The effect of common foreign ions in the developed method was studied in a 50 µg/mL Fe (III) solution and summarised in [Table 1]. Interfering metals Cr^{+6} and Cu^{+2} were masked using sodium diethyldithiocarbamate and sodium thiosulphate, respectively.

3.10 Analytical figure of merits

Various analytical figures of merit for the VA-DLLME method, coupled with UV-visible spectrophotometry, were determined under optimal conditions[Table 2]. The calibration graph was linear in the range of 7.0 µg/L to 70.0 µg/LofFe(III) ions. The correlation coefficient (r^2) of the calibration curve equation was 0.999. The intraday relative standard deviation (RSD) was calculated for 10 replicate measurements using 50 µg/L of Fe (III) and found to be 2.11%. The limit of detection and limit of quantification were calculated using the formulas 3.3σ and 10σ, respectively, and found to be 1.86 µg/L and 5.63 µg/L, demonstrating the method's capability for detecting trace levels of Fe(III) ions. The enrichment factor was determined to be 40.

3.11 Comparison with reported methods:

Table 3 compares our method with other reported DLLME methods coupled with UV-visible spectrophotometers for estimating Fe (III) in various water samples, wine samples, and food samples. Our attempt is the first to utilise VA-DLLME with DES as an extractant for the determination of Fe (III) in the samples of eye shadow. The present work demonstrates a competitive linear range of 7.0 µg/L to 70.0µg/L with a comparatively lower LOD of 1.86µg/L. In the proposed method, environment-friendly DES and vortex assistance align with green analytical principles.

3.12 Application of method:

This developed analytical method was used to determine iron in four different eyeshadow samples collected from Boisar (Maharashtra, India). A sample of 4.0 g was weighed, mixed with a mixture of ethanol and water and digested for 15 minutes. The digested solution was then cooled, centrifuged, and the supernatant liquid was collected and diluted to the required volume with double-distilled water. The solution was then analysed by the VA-DLLME method, and data for four individual determinations is summarised in Table 4. The amount of iron content found in eyeshadows was approximately 8.58 µg/L which found to be within permissible limit.

IV. CONCLUSION

This work introduces a precise, sensitive, easy to use technique for quantifying trace concentrations of Fe(III) ions in eyeshadow samples by vortex-assisted dispersive liquid-liquid microextraction (VA-DLLME) combined with UV-visible spectrophotometry. The use of 1,5-diphenylcarbazone (1,5-DPC) as a chelating agent shown efficacy in the preconcentration of Fe(III) ions, facilitating enhanced sensitivity. Our approach to analysing iron in eyeshadows is innovative. The comparison results in Table 3 indicates that VA-DLLME utilising DES as the extraction solvent shows considerable promise for precisely measuring iron content in eye shadows. The approach demonstrates significant advantages, including simplicity, an extensive linearity range, and elevated recovery rates, hence providing dependable quantification. Moreover, in this microextraction technique, DES is used as an extraction solvent, and dispersion is done with the help of a vortex, which lowers the waste generation, making the proposed method a green analytical method for determining chromium in eyeshadow samples. In summary, this method combines analytical reliability, environmental sustainability, and cost-effectiveness, making it convenient for routine analysis of chromium in eye shadow.

Figures and Tables

Figure1. The IR spectra of deep eutectic solvent:

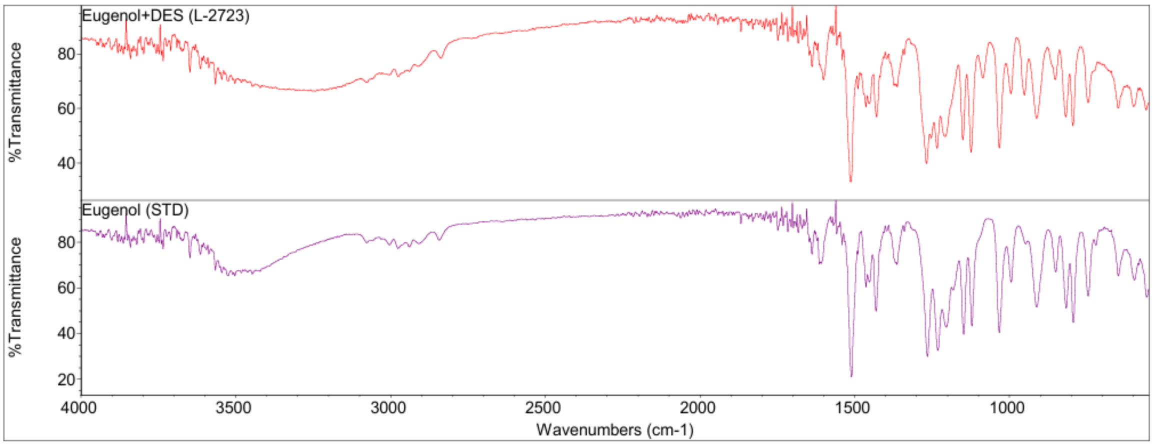
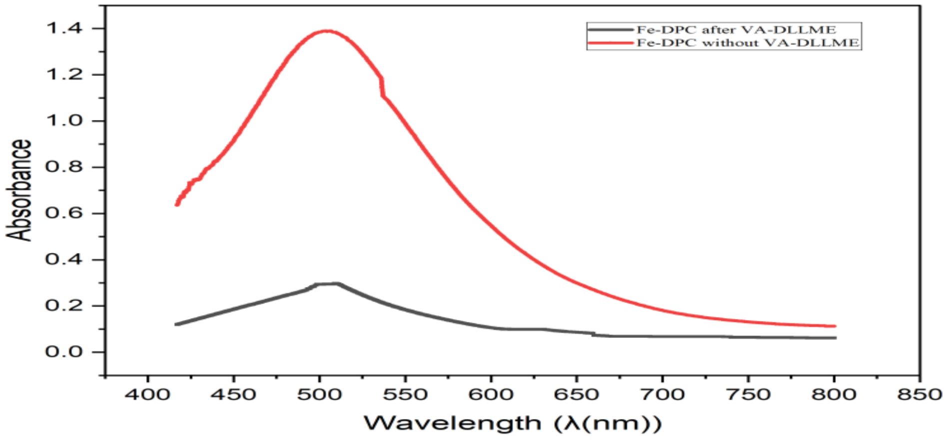
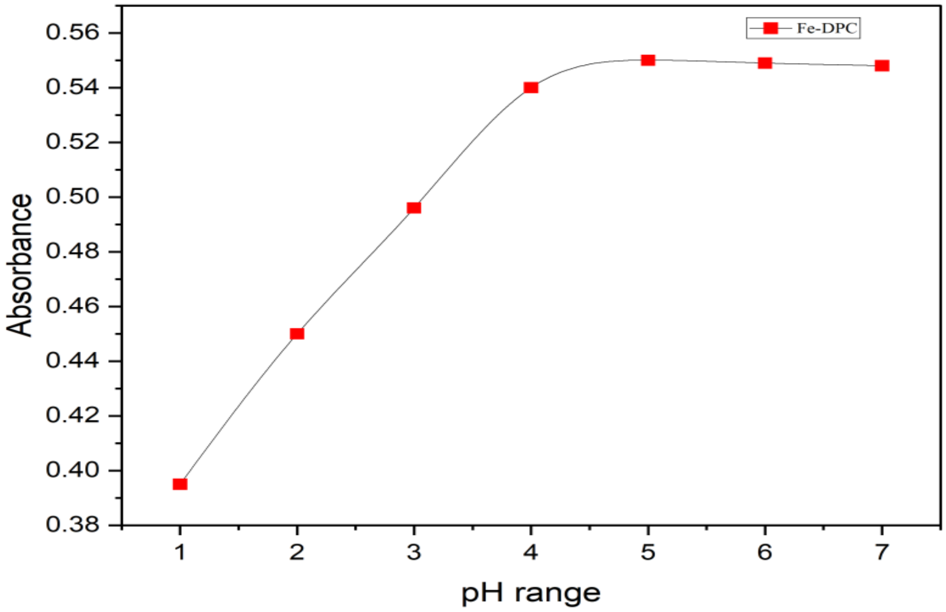


Figure2. Absorption spectra for Fe-DPC complex after and without VA-DLLME



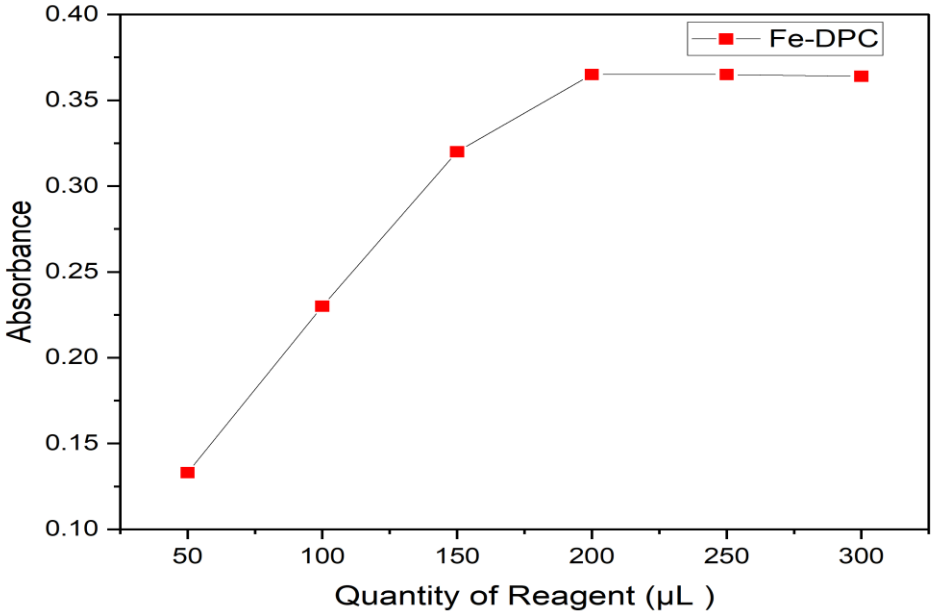
Conditions: Concentration of Fe(III) ions:50 µg/L, pH:5.0, DPC: 2% w/v, Vortex: 0.5 minutes, Centrifugation: 1.0 minutes, DES volume: 250 µL.
VA-DLLME: Vortex Assisted Dispersive Liquid-Liquid Microextraction, DPC:1,5-Diphenylcarbazide, DES: Deep Eutectic Solvent,
The error bars represent the standard deviation (n=3)

Figure 3 Effect of pH



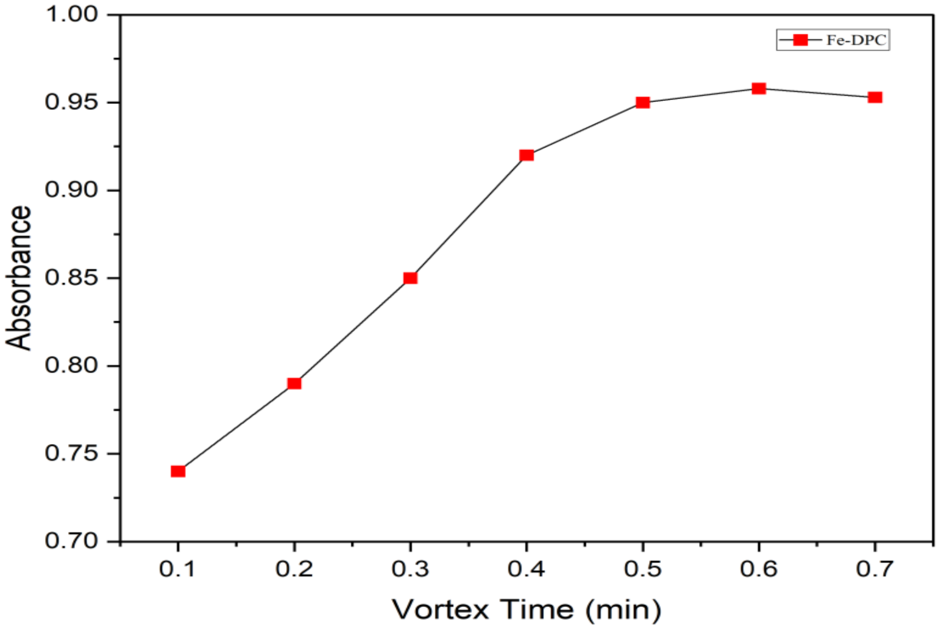
Conditions: λ_{max} : 510 nm, Concentration of Fe(III) ions: 50 µg/L, DPC: 2% w/v, Vortex : 0.5 minutes, Centrifugation: 1.0 minutes, DES volume: 250 µL
VA-DLLME: Vortex Assisted Dispersive Liquid-Liquid Microextraction, DPC:1,5-Diphenylcarbazide, DES: Deep Eutectic Solvent,
The error bars represent the standard deviation (n=3)

Figure 4 Optimising the volume of chelating reagent.



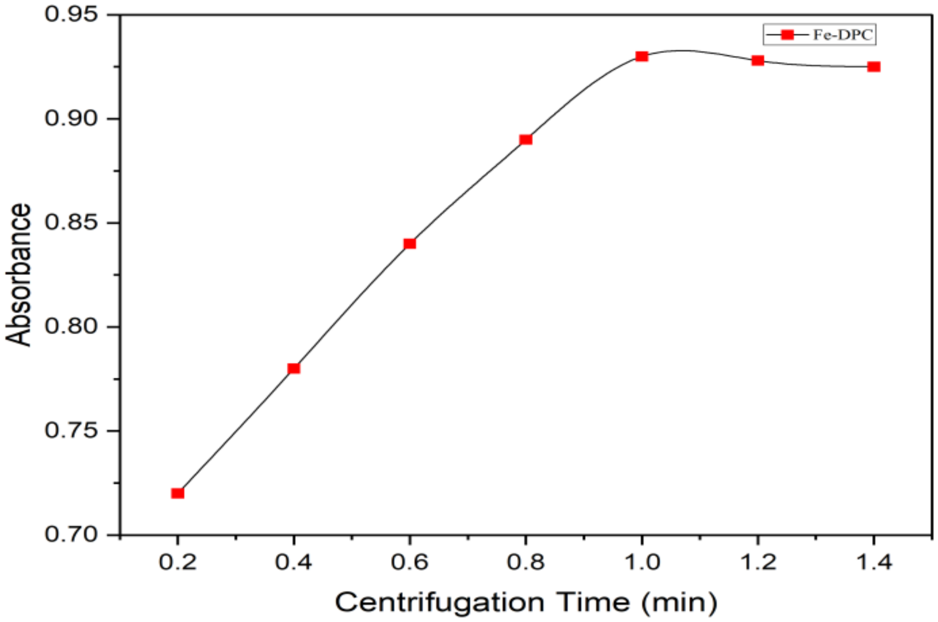
Conditions: λ_{max} : 510 nm, Concentration of Fe(III) ions: 50 µg/L, pH :5.0, DPC: 2% w/v, Vortex : 0.5 minutes, Centrifugation: 1.0 minutes, DES volume: 250 µL
VA-DLLME: Vortex Assisted Dispersive Liquid-Liquid Microextraction, DPC:1,5-Diphenylcarbazide, DES: Deep Eutectic Solvent,
The error bars represent the standard deviation (n=3)

Figure 5 Effect of vortex time.



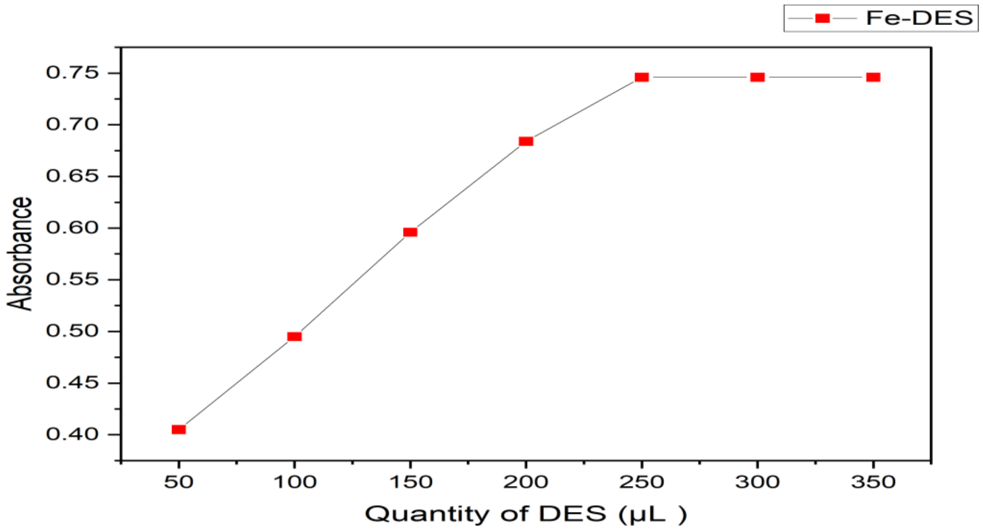
Conditions: λ_{max} : 510 nm, Concentration of Fe(III) ions: 50 µg/L, pH :5.0, DPC: 2% w/v, Centrifugation: 1.0 minutes, DES volume: 250 µL
VA-DLLME: Vortex Assisted Dispersive Liquid-Liquid Microextraction, DPC:1,5-Diphenylcarbazide, DES: Deep Eutectic Solvent,
The error bars represent the standard deviation (n=3)

Figure 6 Effect of Centrifugation time.



Conditions: λ_{max} : 510 nm, Concentration of Fe(III) ions: 50 µg/L, pH :5.0, DPC: 2% w/v, Vortex : 0.5 minutes, DES volume: 250 µL
VA-DLLME: Vortex Assisted Dispersive Liquid-Liquid Microextraction, DPC:1,5-Diphenylcarbazide, DES: Deep Eutectic Solvent,
The error bars represent the standard deviation (n=3)

Figure 7 Effect of DES volume



Conditions: λ_{max} : 510 nm, Concentration of Fe(III) ions: 50 µg/L, pH :5.0, DPC: 2% w/v, Vortex : 0.5 minutes, Centrifugation: 1.0 minutes
VA-DLLME: Vortex Assisted Dispersive Liquid-Liquid Microextraction, DPC:1,5-Diphenylcarbazide, DES: Deep Eutectic Solvent,
The error bars represent the standard deviation (n=3)

Table 1 Effect of common foreign ions for determination of 50 µg/L of Fe (III) with 1,5-diphenylcarbazone. (Relative error ±5%)

Interference	Interference to metal ion ratio	Recovery %
Ni^+	1:4	95.6
Zn^+	1:8	94.5
Co^+	1:8	93.5
Ba^+	1:6	103.7
Cd^+	1:5	113.4
Hg^+	1:4	106.6
Mg^+	1:2	101.1
Mn^+	1:4	99.5
$^aCr^{+6}$	1:1	99.65
$^bCu^{2+}$	1:1	99.80
So_4^-	1:4	105.8
Cl^-	1:4	104.1
F^-	1:4	110.1
Pb^+	1:4	105.8

[a] Masked with 0.6 mg Sodium diethyldithiocabarmate,
[b] Masked with 0.4 mg sodium thiosulphate

Table 2 Figures of merit

Parameter	Analytical Feature
Linear range	7.0 µg/L to 70.0 µg/L
r^2	0.999
Limit of detection (LOD)	1.86 µg/L
Limit of quantification (LOQ)	5.63 µg/L
Slope	0.013
Intercept	0.329
Enrichment factor	40
Standard Deviation	0.016
RSD	2.11 %

*LOD and LOQ based on 3.3 σ and 10 σ criterion, respectively. *r^2correlation coefficient

Table.3 Comparison of different analytical techniques with present method for determination of Iron.

Separating/ Analytical techniques	Linear Range, µg/L	[a]LOD, µg/L	[b]RSD %	[c]EF	Samples	Solvents	Reference no
DLLME- UV-Visible spectrophotometry	25–1000	7.5	1.2 %	-	Water Sample	Chloroform methanol	38
DLLME- Digital image colorimetric	47-1000	14.1	3.75 %	-	Water and Food Sample	Methanol, Chloroform	39
DLLME- UV-Visible spectrophotometry	750 – 2500	200	Below 7%.	-	Wine sample	C_2Cl_4 Acetonitrile	40
DLLME- UV-Visible spectrophotometry	20-250	6.1	Lower than 12%	-	Water Sample	1,2-dichlorobenzene, ethanol	41
DLLME- UV-Visible spectrophotometry	5-400	1.5	3.6%	10	Water and Food Sample	Ethanol, Carbon tetrachloride	42
DLLME- UV-Visible spectrophotometry	7.0-70	1.86	2.11%	40	Eye-shadow sample	DES	Present work

[a]LOD- Limit of Detection, [b]RSD- Relative Standard Deviation, [c]EF-Enrichment Factor

Table 4. Determination of Fe (III) in eye-shadow samples.

Eye-Shadow Samples 4.0 g each	Iron amount		Recovery (%)
	Spiked in µg/L	Found * in µg/L	
Sample 1	0	20.81 ±0.19	-
	05	25.07 ±0.39	101
	10	30.46 ±0.07	102
Sample 2	0	20.02 ±0.50	-
	05	25.9 ±0.13	101
	10	30.39 ±0.19	99
Sample 3	0	20.83 ±0.24	-
	05	25.64 ±0.36	99
	10	30.43 ±0.43	100
Sample 4	0	20.83 ±0.18	-
	05	25.64 ±0.52	99
	10	30.43 ±0.09	100

*Mean ± Standard deviation (n=5)

V. ACKNOWLEDGEMENTS

Corresponding author is highly grateful to Sonopant Dandekar Arts, V.S. Apte Commerce and M.H. Mehta Science College, Palghar, Maharashtra, India for providing financial support under in-house minor research project grant.

REFERENCES

[1] M.S. Abed, A.A. Moosa, and M.A. Alzuhairi, Journal of Hazardous Materials Advances **13**, 100390 (2024).

[2] In Rheology Essentials of Cosmetic and Food Emulsions (Springer-Verlag, Berlin/Heidelberg, 2006), pp. 155–160.

[3] Lv, V.; Pp, A.; Farsana, K.; T, K.; V, S.; TK, A.B.Curr.Res.Pharm.Sci.13, 83 (2023).

[4] E. Guerra, M. Llompart, and C. Garcia-Jares, Cosmetics 5, 47 (2018).

[5] H.A.M. Ahmed, K.M.A. Al-Qahtani, H. Emara, M.N. Janjua, N. Alhafez, and M.B. Al-Otaibi, Asian J. Chem. 29, 1441 (2017).

[6] C.M.A. Iwegbue, F.I. Bassey, G. Obi, G.O. Tesi, and B.S. Martincigh, Toxicology Reports 3, 464 (2016).

[7] Ibtesam Amer, Alq J Med App Sci 826 (2024).

[8] S. Borowska and M.M. Brzóska, J of Applied Toxicology 35, 551 (2015).

[9] A.B.G. Lansdown, Intern J of Cosmetic Sci 23, 129 (2001).

[10] M.G. Volpe, M. Nazzaro, R. Coppola, F. Rapuano, and R.P. Aquino, Microchemical Journal 101, 65 (2012).

[11] L. Świerczek, B. Cieślik, A. Matysiak, and P. Konieczka, Monatsh Chem 150, 1675 (2019).

[12] Y.E. Unsal, M. Soylak, M. Tuzen, and B. Hazer, Analytical Letters 48, 1163 (2015).

[13] Q.-W. Zhang, L.-G. Lin, and W.-C. Ye, Chin Med 13, 20 (2018).

[14] S.A. Arain, T.G. Kazi, H.I. Afridi, M.S. Arain, A.H. Panhwar, N. Khan, J.A. Baig, and F. Shah, Ecotoxicology and Environmental Safety 126, 186 (2016).

[15] S. Dugheri, N. Mucci, A. Bonari, G. Marrubini, G. Cappelli, D. Ubiali, M. Campagna, M. Montalti, and G. Arcangeli, Acta Chromatographica 32, 69 (2020).

[16] T. Vander Hoogerstraete, B. Onghena, and K. Binnemans, J. Phys. Chem. Lett. 4, 1659 (2013).

[17] A. Rohanifar, L.B. Rodriguez, A.M. Devasurendra, N. Alipourasiabi, J.L. Anderson, and J.R. Kirchhoff, Talanta 188, 570 (2018).

[18] J.M. Kokosa, TrAC Trends in Analytical Chemistry 71, 194 (2015).

[19] R. Akramipour, M.R. Golpayegani, S. Gheini, and N. Fattahi, Talanta 186, 17 (2018).

[20] M. Rezaee, Y. Yamini, and M. Faraji, Journal of Chromatography A 1217, 2342 (2010).

[21] A. Sixto, A. Mollo, and M. Knochen, Journal of Food Composition and Analysis 82, 103229 (2019).

[22] T.S. Seeger, P.D. Vecchia, E.Q. Machado, K. Reinke, M.F. Mesko, and F.A. Duarte, J. Braz. Chem. Soc. (2017).

[23] D. Martínez, D. Torregrosa, G. Grindlay, L. Gras, and J. Mora, Talanta 176, 374 (2018).

[24] M. Naseri, Talanta 75, 56 (2008).

[25] Q. Han, X. Yang, Y. Huo, J. Lu, and Y. Liu, Separations 10, 93 (2023).

[26] M. Rouhi, J. Abolhasani, M.R. Afshar Mogaddam, and M.T. Vardini, Chem. Pap. 77, 7421 (2023).

[27] W.A. Soomro, M.Y. Khuhawar, T.M. Jahangir, M.F. Lanjwani, Z.A. Bhatti, R.-Z. Brohi, and I.K. Rind, Environ Monit Assess 197, 235 (2025).

[28] Y. Dilip, P. Laxman, J. Suhas, N. Arundhati, and C. Mrunmayi, International Journal of Environmental Analytical Chemistry 1 (2024).

[29] M. Tavakoli, M.R. Jamali, and A. Nezhadali, Analytical Letters 54, 2863 (2021).

[30] A. Mostafa, H. Shaaban, A.M. Alqarni, M. Alghamdi, S. Alsultan, J. Saleh Al-Saeed, S. Alsaba, A. AlMoslem, Y. Alshehry, and R. Ahmad, Microchemical Journal 183, 107976 (2022).

[31] H. Wei, J. Yang, H. Zhang, and Y. Shi, Chem. Res. Chin. Univ. 30, 368 (2014).

[32] X. Jia, Y. Han, C. Wei, T. Duan, and H. Chen, J. Anal. At. Spectrom. 26, 1380 (2011).

[33] K. Sharafi, N. Fattahi, M. Pirsaheb, H. Yarmohamadi, and M. Fazlzadeh Davil, Intern J of Cosmetic Sci 37, 489 (2015).

[34] Ş. Saçmacı and M. Saçmacı, Applied Organom Chemis 31, e4081 (2017).

[35] H. Haghgoo Qezelje, M. Rajabi, E. Parsa, S. Ghanbari Adivi, M. Shahi, A. Asghari, M. Bazregar, and A. Hosseini-Bandegharaei, CAC 20, 418 (2024).

[36] S. Shafique, A.S. Belousov, R. Rashid, I. Shafiq, K.H.H. Aziz, N. Riaz, M.S. Khan, A. Shaheen, M. Ishaq, P. Akhter, and M. Hussain, Journal of Molecular Liquids 419, 126769 (2025).

[37] C. Wang, S. Ji, Q. Wu, C. Wu, and Z. Wang, Journal of Chromatographic Science 49, 689 (2011).

[38] A.B. Tabrizi, Journal of Hazardous Materials 183, 688 (2010).

[39] B. Peng, G. Chen, K. Li, M. Zhou, J. Zhang, and S. Zhao, Food Chemistry 230, 667 (2017).

[40] J.V. Maciel, B.M. Soares, J.S. Mandlate, R.S. Picoloto, C.A. Bizzi, E.M.M. Flores, and F.A. Duarte, J. Agric. Food Chem. 62, 8340 (2014).

[41] E.R. Pereira, B.M. Soares, J.V. Maciel, S.S. Caldas, C.F.F. Andrade, E.G. Primel, and F.A. Duarte, Anal. Methods 5, 2273 (2013).

[42] B. Peng, Y. Shen, Z. Gao, M. Zhou, Y. Ma, and S. Zhao, Food Chemistry 176, 288 (2015).