RESEARCH PAPER

SURFACTANT ASSEMBLY-ASSISTED WATER QUALITY ANALYSIS OF THE SHIVNATH RIVER, CHHATTISGARH, INDIA:AN ECO-FRIENDLY ANALYTICAL APPROACH

Dr.Pratibha S. Kurup*[1], Dr. Preeti Nandkumar[2], Mrs Swapnil Goswami[3]
[1]Professor,Department of Chemistry, Rungta International Skills University,Bhilai Corresponding author
e-mail: pratibha.sureshkurup@rungta.org
[2]Associate Professor,Department of Chemistry, Christan College of Engineering and Technology,Bhilai,
nandinipreeti@gmail.com
[3]Reseacrh Scholar,Department of Chemistry,Bharti Vishwavidhyalaya,Durg, situ_478@yahoo.com

1. Abstract

Rivers draining rapidly at the catchments of central India due to industrializing and urbanizing,includes the Shivnath River – the principal tributary of the Mahanadi in Chhattisgarh – are increasingly stressed by domestic sewage, agricultural runoff and industrial discharge. Conventional trace-metal analysis conflicts with the goals of green analytical chemistry.of waters typically relies on toxic chelating solvents and energy-intensive instrumentation. This paper describes and applies a surfactant assembly-assisted (cloud point extraction, CPE) analytical protocol, using the non-ionic surfactant Triton X-114 as an eco-friendly extraction and preconcentration medium, coupled with UV-Visible spectrophotometry, for the multi-analyte determination of physicochemical water quality and trace-metal contamination (Fe, Cu, Pb and Cr(VI)) of the Shivnath River across six stations spanning the Rajnandgaon–Durg reach. The method was optimised for surfactant concentration, pH, chelating-agent concentration, equilibration temperature/time and ionic strength, and validated for linearity, limit of detection (LOD), limit of quantification (LOQ), preconcentration factor, precision and recovery, with cross-validation against flame atomic absorption spectrometry (FAAS). A composite Water Quality Index (WQI) computed from eight physicochemical parameters showed a consistent upstream-to-downstream deterioration, from 'poor' near the river's upper reaches to 'unfit for drinking without treatment' near the Durg urban-industrial belt, mirroring a parallel increase in Fe, Cu, Pb and Cr(VI) concentrations. A greenness assessment (AGREE metric) confirmed the CPE-UV-Vis method offers a substantially smaller environmental and safety footprint than conventional solvent-extraction/FAAS approaches while retaining comparable accuracy (mean bias ≤ 4%). The results demonstrate that surfactant-assembly-assisted analysis is a practical, low-cost, and sustainable strategy for routine river water-quality surveillance in resource-limited regional laboratories, and provide a station-resolved baseline dataset for the Shivnath River that can support future pollution-control planning.

Keywords: Cloud Point Extraction; Triton X-114; Uv–Vis Spectrophotometry; Green Analytical Chemistry; Trace Metals; Shivnath River; Water Quality Index; Environmental Monitoring.

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1. Introduction

The Shivnath River, the second-largest tributary of the Mahanadi River, which flows for approximately 290 km through Rajnandgaon, Durg, Balod and Bemetara districts of Chhattisgarh and is considered as lifeline of the state,It supplies water for domestic use, irrigation, fisheries and industry [1–3]. over the last decade Field surveys conducted have repeatedly reported deteriorating water quality along its middle and lower reaches, with pH, turbidity, calcium, nitrate, BOD, COD and faecal-coliform levels exceeding BIS/WHO permissible limits downstream of major towns, attributed to untreated domestic sewage and industrial effluent discharge in the Durg–Bhilai industrial belt [4]. Water quality index (WQI) assessments for the Durg district have reported values ranging from about 29 to 92 across pre-monsoon, monsoon and post-monsoon seasons, with the poorest quality consistently recorded in the pre-monsoon period when dilution is lowest [5]. More recent ichthyofaunal and environmental-stressor studies have additionally flagged elevated heavy metals, including mercury and lead, together with nutrient enrichment from agricultural runoff, as ongoing threats to the river's ecological integrity [6,7].

Trace-metal monitoring in such river systems conventionally relies on liquid–liquid extraction with hazardous organic solvents (chloroform, carbon tetrachloride, MIBK) prior to flame or graphite-furnace atomic absorption spectrometry (FAAS/GFAAS) or ICP-OES/MS. Though the methods are sensitive, these approaches are costly, generate hazardous organic waste, and are poorly suited to routine surveillance by regional laboratories in developing regions. Green analytical chemistry (GAC) has therefore promoted surfactant-based cloud point extraction (CPE) as an alternative separation and preconcentration strategy [8–10]. In CPE, an aqueous solution of a non-ionic surfactant (e.g., Triton X-100/X-114, polyoxyethylene glycol alkylphenyl ethers) is heated above its cloud-point temperature, causing the surfactant molecules to self-assemble into micelles that aggregate into a small-volume, surfactant-rich phase; hydrophobic metal–chelate complexes formed in situ partition preferentially into this phase, which is then separated by simple centrifugation, eliminating the need for volatile organic solvents [9,11]. The technique has been successfully applied to the

preconcentration and spectrophotometric or spectrometric determination of Fe, Cu, Cr, Pb, Cd, Hg, Sb, Bi and other analytes in waters, foods and biological matrices, typically achieving preconcentration factors of 20–50-fold with detection limits in the low-μg L^{-1} range [10,12–16].

The present study is the application of surfactant assembly-assisted (CPE-UV-Vis) protocol, in combination with standard physio-cochemical methods, to characterise water quality along a six-station transect of the Shivnath River spanning its upper reaches in Rajnandgaon district to the Durg urban-industrial belt. The specific objectives was to: (i) develop and optimize a Triton X-114-mediated CPE procedure for Fe(III), Cu(II), Pb(II) and Cr(VI) with UV-Visible detection; (ii)Validate and Cross Check the method's analytical figures of merit and cross-check it against FAAS; (iii) Characterize twelve physicochemical parameters and four trace metals at each station; (iv) Calculate WQI and compare it with BIS/CPCB drinking- and bathing-water criteria; and (v) Evaluate the 'greenness' of method relative to conventional solvent-extraction/FAAS analysis using the AGREE metric, so as to demonstrate a low-cost, low-waste analytical strategy suited to routine river-monitoring programmes in resource-limited settings.

2. Study Area and Sampling Sites

Six sampling stations (S1–S6) were selected along approximately 95 km of the Shivnath River, progressing from a comparatively undisturbed reach near its upper course in Rajnandgaon district (S1) through the Rajnandgaon town barrage (S2), an agriculturally dominated reach at Mahamara Anicut (S3), a semi-urban reach at Rasmara Ghat (S4), the Durg city barrage adjacent to the water-treatment-plant intake (S5), and a downstream confluence zone near Somnath where the Shivnath receives the Kharun River before joining the Mahanadi (S6). Station coordinates and land-use context are given in Table 1.

Table 1. Sampling stations along the Shivnath River (Rajnandgaon–Durg reach).

Station_ID	Location	Latitude_N	Longitude_E	Description
S1	Chhirpani (near origin),Dongargaon block, Rajnandgaon	20.9721	80.9382	Upstream/ least disturbed
S2	Rajnandgaon town barrage	21.0974	81.0294	Urban/domestic discharge
S3	Mahamara Anicut, Rajnandgaon-Durg border	21.1782	81.1856	Agricultural runoff zone
S4	Rasmara Ghat, Durg district	21.2016	81.2703	Semi-urban, mixed land use
S5	Durg City Barrage (near Kutelabhata WTP intake)	21.1904	81.2849	Major urban / industrial belt
S6	Somnath confluence zone(Shivnath-Kharun, downstream of Durg)	21.2451	81.3762	Downstream / pre-confluence with Mahanadi

3. Materials and Methods

3.1 Chemicals and Reagents

Triton X-114 (non-ionic surfactant, cloud point ~23°C) was used as the extraction medium. 1-(2-Pyridylazo)-2-naphthol (PAN) was used as the chelating agent for Fe(III), Cu(II) and Pb(II); 1,5-diphenylcarbazide (DPC) was used for Cr(VI). Buffer solutions (acetate, pH 3–6; phosphate, pH 6–8) were used for pH adjustment, and analytical-grade NaCl was used to study ionic-strength effects. All reagents were of analytical reagent grade; solutions were prepared in ultrapure (18.2 MΩ·cm) water. Stock metal solutions (1000 mg L^{-1}) were used to prepare working standards by serial dilution. Glassware was soaked in 10% v/v HNO_3 and rinsed with ultrapure water prior to use.

3.2 Instrumentation

A UV-Visible spectrophotometer (1 cm quartz microcuvette, scan range 400–600 nm) was used for absorbance measurement of the surfactant-rich phase. A thermostatted water bath, bench-top centrifuge (4000 rpm), digital pH meter, conductivity/TDS meter, turbidimeter, and a flame atomic absorption spectrophotometer (FAAS, air–acetylene flame) for cross-validation were also used. Dissolved oxygen was measured by the Winkler titrimetric method, and BOD_5/COD by standard 5-day incubation and open-reflux dichromate methods, respectively, following APHA (23rd edn.) protocols [17].

3.3 Sampling and Preservation

Grab sampling method was used for sampling.Surface-water samples (0–0.3 m depth) were collected in triplicate I.e. Three independent grab samples were collected at each station and independently processed and analyzed at each station in pre-cleaned polyethylene bottles during the pre-monsoon campaign, following APHA guidelines. Samples for metal analysis were filtered (0.45 μm) and acidified to pH < 2 with ultrapure HNO_3; samples for physicochemical analysis were stored at 4°C and analysed within 24–48 h. DO and pH were measured in situ.

3.4 Cloud Point Extraction (Surfactant Assembly) Procedure

The CPE procedure comprised the following steps:

A 10 mL aliquot of filtered water sample (or standard) was placed in a centrifuge tube and the pH adjusted to the

optimum value with buffer.
2. The chelating agent (PAN or DPC, as appropriate) was added at its optimised concentration and allowed to react for 5 min to form the hydrophobic metal–chelate complex.
3. Triton X-114 was added to the optimised concentration (% w/v) and the tube was equilibrated in a thermostatted water bath at the optimum temperature for the optimum time, inducing micellar self-assembly and clouding.
4. Phase separation was achieved by centrifugation (4000 rpm, 10 min); the dilute aqueous phase was decanted, and the residual surfactant-rich phase was cooled in ice to increase its viscosity for handling.
5. The surfactant-rich phase was diluted to a fixed micro-volume with acidified ethanol to reduce viscosity, and its absorbance was measured against a reagent blank processed identically.
6. Analyte concentration was obtained from a matrix-matched calibration curve constructed by subjecting standards to the same CPE procedure.

3.5 Physicochemical Analysis

pH, electrical conductivity (EC), total dissolved solids (TDS), turbidity, dissolved oxygen (DO), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total hardness, chloride, nitrate, sulphate and fluoride were determined following APHA Standard Methods for the Examination of Water and Wastewater [17].

3.6 Method Validation and Greenness Assessment

Linearity, LOD (3.3σ/slope), LOQ (10σ/slope), preconcentration factor and intraday precision (%RSD, n = 6) were determined for each analyte. Accuracy was assessed by spike-recovery experiments at two concentration levels and by parallel analysis of a subset of samples by FAAS. Method 'greenness' was benchmarked against conventional solvent-extraction/FAAS analysis using the AGREE (Analytical GREEnness) semi-quantitative scoring approach [18], considering reagent toxicity, waste generation, energy use, analysis time, and operator safety.

3.7 Water Quality Index (WQI)

A weighted arithmetic WQI was calculated from eight parameters (pH, DO, BOD, TDS, total hardness, chloride, nitrate and turbidity) using BIS/CPCB standards as the parameter denominators (Sn) and unit weights Wn = K/Sn, where K = 1/Σ(1/Sn), following the standard Horton–NSF weighted-arithmetic procedure [19,20]. Sub-indices (qn) were computed relative to the ideal value for pH (7.0) and DO (14.6 mg L^{-1}) and relative to zero for the remaining parameters; the overall WQI = Σ(qn·Wn)/ΣWn was classified as excellent (<25), good (25–50), poor (50–75), very poor (75–100) or unfit for drinking without conventional treatment (>100).

$$WQI=\sum WnQn/\sum Wn$$

where: $Wn=K/Sn$ $K= 1/\sum(1/Sn)$

The quality rating is $Qn=(Vn-Vio)/(Sn-Vio)\times100$

For DO, because higher DO is desirable: $Q DO=(14.6-VDO)/(14.6-5)\times100$

3.8 Statistical Analysis

Results are reported as mean ± standard deviation of triplicate measurements. Pearson correlation coefficients were computed between physicochemical and trace-metal parameters (station means) to identify co-varying pollution sources.

4. Results and Discussion – Method Development and Validation

4.1 Optimisation of Cloud Point Extraction Parameters

Single-factor-at-a-time optimisation (Table 2) identified 0.10–0.15% w/v Triton X-114, pH 6, 6×10^{-4} M PAN (or equivalent DPC concentration for Cr(VI)), 45–50°C equilibration temperature, 15–20 min equilibration time, and 0–1% w/v NaCl as the optimum conditions, giving extraction efficiencies of 96–98%. Extraction efficiency declined at surfactant concentrations above 0.20% w/v due to an increase in surfactant-rich-phase volume (diluting the analyte), at pH values away from the optimum due to incomplete complex formation or competing hydrolysis, and at NaCl concentrations above ~2% due to salting-out effects that altered micelle aggregation number.

Table 2a. Effect of Triton X-114 concentration on extraction efficiency (pH 6, PAN 6×10^{-4} M, 45°C, 15 min)

Triton_X114_%_w_v	Extraction_Efficiency_%
0.02	54
0.05	71
0.1	92
0.15	96
0.2	95
0.3	90

Table 2b. Effect of pH on extraction efficiency..

pH	Extraction_Efficiency_%
3	38
4	62
5	85
6	97
7	94

8	80
9	55

Table 2c. Effect of PAN concentration on extraction efficiency.

PAN_x1e-4_M	Extraction_Efficiency_%
1	48
2	74
4	93
6	98
8	97
10	96

Table 2d. Effect of equilibration temperature on extraction efficiency.

Equilibration_Temp_C	Extraction_Efficiency_%
35	60
40	82
45	97
50	98
55	96
60	93

Table 2e. Effect of equilibration time on extraction efficiency.

Equilibration_Time_min	Extraction_Efficiency_%
5	55
10	79
15	96
20	98
25	98
30	97

Table 2f. Effect of ionic strength (NaCl) on extraction efficiency.

NaCl_%_w_v	Extraction_Efficiency_%
0	97
1	98
2	96
3	90
4	80
5	68

4.2 Analytical Figures of Merit

Under optimised conditions, each analyte showed good linearity ($R^2 \geq 0.997$) over its working range, with preconcentration factors of 35–45-fold and low-µg L^{-1} detection limits (Table 3). Intraday precision (%RSD, n = 6) was ≤ 3.6% for all analytes, indicating good method repeatability.

Table 3. Analytical figures of merit for CPE-UV-Vis determination of Fe(III), Cu(II), Pb(II) and Cr(VI).

Analyte	Chelating_Agent	Wavelength_nm	Linear_Range_mg_L	Regression_Equation	R2	LOD_mg_L	LOQ_mg_L	Preconcentration_Factor	Intraday_RSD_%
Fe(III)	PAN	510	0.05-2.00	A=0.4231C+0.0102	0.99987	0.012	0.039	42	3.1
Cu(II)	PAN	555	0.05-2.50	A=0.3765C+0.0087	0.99981	0.015	0.048	38	2.8

Pb(II)	PAN	470	0.10-3.00	A=0.2894C+0.0064	0.9976	0.028	0.092	35	3.6
Cr(VI)	1,5-diphenylcarbazide	540	0.02-1.50	A=0.5123C+0.0055	0.99992	0.006	0.02	45	2.4

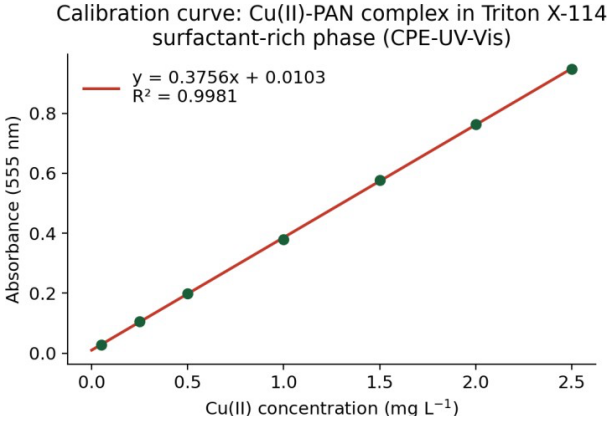

Figure 1. Representative calibration curve for Cu(II)–PAN complex in the Triton X-114 surfactant-rich phase (555 nm).

4.3 Accuracy: Spike-Recovery and Cross-Validation Against FAAS

Spike-recovery experiments at two concentration levels gave recoveries of 94–102% with RSD ≤ 3.6% for all four analytes (Table 4), confirming the method's accuracy in the river-water matrix. Parallel analysis of a station subset by FAAS agreed with the CPE-UV-Vis results within ≤ 4.0% mean relative difference (Table 5), with no systematic bias evident, supporting the suitability of the surfactant-assembly method as a low-cost alternative to FAAS for routine screening.

Table 4. Spike-recovery study for Fe(III), Cu(II), Pb(II) and Cr(VI) in Shivnath River water (n = 3)

Analyte	Spiked_Conc_mg_L	Found_Conc_mg_L	Recovery_%	RSD_%
Fe(III)	0.2	0.196	98	2.6
Fe(III)	0.5	0.512	102.4	2.1
Cu(II)	0.2	0.191	95.5	3
Cu(II)	0.5	0.505	101	2.4
Pb(II)	0.2	0.188	94	3.4
Pb(II)	0.5	0.498	99.6	2.9
Cr(VI)	0.2	0.203	101.5	1.9
Cr(VI)	0.5	0.507	101.4	2

Table 5. Cross-validation of CPE-UV-Vis against FAAS for a representative station subset.

Station_ID	Analyte	CPE_UVVis_mg_L	FAAS_mg_L	Percent_Difference
S2	Fe	0.254	0.262	-2.7
S4	Fe	0.440	0.451	-2.4
S6	Fe	0.507	0.518	-2.1
S2	Cu	0.0207	0.0212	-2.3
S4	Cu	0.0380	0.0388	-2.1
S6	Cu	0.0431	0.0440	-2
S2	Pb	0.0118	0.0123	-4
S4	Pb	0.0240	0.0247	-2.8
S6	Pb	0.0270	0.0278	-2.9

4.4 Greenness Assessment

The AGREE-based comparison (Table 6) shows the CPE-UV-Vis protocol scoring markedly higher than a conventional solvent-extraction/FAAS workflow across nearly every greenness criterion, principally reflecting the elimination of chlorinated/aromatic extraction solvents, reduced reagent and sample volumes, and lower energy demand — consistent with the broader literature positioning CPE as a core green-chemistry preconcentration strategy [9,18].

Table 6. AGREE greenness scores (0–1 scale; higher = greener) for CPE-UV-Vis versus conventional solvent-extraction/FAAS analysis.

Criterion	CPE-UV-Vis (this work)	Conventional FAAS/solvent extraction

Sample amount / waste generated	0.8	0.54
Toxicity of reagents	0.87	0.3
Energy consumption	0.74	0.5
Analysis time	0.6	0.64
Automation potential	0.6	0.6
Number of analytical steps	0.71	0.57
Sample/reagent volume	0.84	0.44
Operator safety	0.8	0.4
Overall AGREE score	0.77	0.51

5. Results and Discussion – Field Application to the Shivnath River

5.1 Physicochemical Water Quality

Physicochemical parameters showed a consistent, monotonic deterioration from the upstream station (S1) to the Durg urban-industrial belt (S5), with a slight improvement at the downstream confluence station (S6) attributable to dilution by the Kharun River (Table 7). pH remained slightly alkaline (7.6–8.0) at all stations, within the BIS acceptable range. Dissolved oxygen declined from 7.6 mg L^{-1} at S1 to 4.9 mg L^{-1} at S5, while BOD and COD rose roughly three-fold over the same transect, consistent with increasing organic-matter loading from domestic sewage and reduced self-purification capacity nearer Durg city, in agreement with earlier reports of downstream water-quality decline in this reach [4,5]. Turbidity, chloride, nitrate, sulphate, total hardness and TDS followed the same increasing trend, though all remained below BIS maximum-permissible limits except turbidity and BOD at S4–S6 (Table 8).IS 10500:2012 for drinking-water comparison and CPCB criteria for surface-water quality classification was used.

Table 7a. Physicochemical water quality parameters (group 1) at six Shivnath River stations, pre-monsoon campaign (mean ± SD, n = 3).

Station	pH	EC (µS/cm)	TDS (mg/L)	Turbidity (NTU)	DO (mg/L)	BOD (mg/L)	COD (mg/L)
S1	7.60 ± 0.14	278.77 ± 15.53	195.53 ± 1.40	3.27 ± 0.15	7.45 ± 0.51	1.07 ± 0.05	8.47 ± 0.40
S2	7.56 ± 0.46	333.70 ± 7.72	228.57 ± 7.02	4.70 ± 0.00	6.90 ± 0.44	1.62 ± 0.05	12.20 ± 0.10
S3	7.35 ± 0.08	409.93 ± 17.61	275.33 ± 6.17	6.37 ± 0.25	6.17 ± 0.16	2.37 ± 0.07	18.30 ± 0.52
S4	7.96 ± 0.40	465.83 ± 24.15	315.67 ± 16.69	8.40 ± 0.50	5.65 ± 0.20	2.99 ± 0.18	25.43 ± 1.19
S5	7.89 ± 0.20	564.93 ± 20.24	363.93 ± 1.50	10.33 ± 0.40	4.87 ± 0.26	3.78 ± 0.14	32.37 ± 2.76
S6	7.85 ± 0.67	534.13 ± 20.96	336.20 ± 6.16	9.03 ± 0.59	5.32 ± 0.22	3.44 ± 0.19	28.03 ± 0.68

Table 7b. Physicochemical water quality parameters (group 2) at six Shivnath River stations, pre-monsoon campaign (mean ± SD, n = 3).

Station	Hardness (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Sulphate (mg/L)	Fluoride (mg/L)
S1	126.37 ± 1.19	17.77 ± 0.25	1.17 ± 0.06	14.63 ± 0.25	0.29 ± 0.01
S2	145.87 ± 3.38	26.30 ± 0.75	2.17 ± 0.12	18.60 ± 1.06	0.34 ± 0.02
S3	168.93 ± 4.65	34.50 ± 1.21	3.37 ± 0.06	23.73 ± 0.80	0.39 ± 0.01
S4	193.80 ± 20.94	46.00 ± 1.32	4.47 ± 0.12	30.53 ± 2.90	0.47 ± 0.02

S5	209.00 ± 6.94	58.70 ± 4.97	6.03 ± 0.15	38.50 ± 1.13	0.58 ± 0.02
S6	195.70 ± 6.60	51.13 ± 2.40	5.63 ± 0.29	34.83 ± 1.83	0.53 ± 0.02

Table 8. BIS 10500:2012 / CPCB permissible limits used for comparison and WQI computation.

Parameter	Permissible_Limit	Standard
pH	6.5-8.5	IS 10500:2012
TDS_mg_L	500 (2000 max permissible)	IS 10500:2012
Turbidity_NTU	1 (5 max permissible)	IS 10500:2012
DO_mg_L	>=4 (Class C, bathing/propagation)	CPCB Designated Best Use
BOD_mg_L	<=3 (Class C)	CPCB Designated Best Use
Total_Hardness_mg_L	200 (600 max permissible)	IS 10500:2012
Chloride_mg_L	250 (1000 max permissible)	IS 10500:2012
Nitrate_mg_L	45	IS 10500:2012
Sulphate_mg_L	200 (400 max permissible)	IS 10500:2012
Fluoride_mg_L	1.0 (1.5 max permissible)	IS 10500:2012

5.2 Trace-Metal Contamination

Fe, Cu, Pb and Cr(VI) concentrations, determined by the validated CPE-UV-Vis method, increased two-to three-fold from S1 to S5 before declining slightly at S6 (Table 9, Figure 3), mirroring the physicochemical trend and indicating a common source of pollutant loading — principally urban and industrial discharge in the Durg belt. Mean Pb(II) concentrations were below the BIS acceptable limit of 0.01 mg L^{-1} , while Fe, Cu and Cr(VI) remained within BIS permissible limits at all stations, though the increasing trend toward S5 warrants continued monitoring given the cumulative and bioaccumulative toxicity of these metals (Table 10).

Station	Fe(III) (mg/L)	Cu (mg/L)	Pb (mg/L)	Cr(VI) (mg/L)
S1	0.18 ± 0.00	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
S2	0.24 ± 0.02	0.02	0.01	0.01
S3	0.38 ± 0.05	0.03	0.02	0.01
S4	0.46 ± 0.03	0.04	0.02	0.01
S5	0.59 ± 0.01	0.05	0.03	0.02
S6	0.49 ± 0.03	0.04	0.03	0.02

Table 9. Trace-metal concentrations (CPE-UV-Vis) at six Shivnath River stations, pre-monsoon campaign (mean ± SD, mg L^{-1}, n = 3).

Parameter	Permissible_Limit	Standard
Fe(III)mg/L	1.0 (0.3 acceptable)	IS 10500:2012
Cu mg/L	1.5 (0.05 acceptable)	IS 10500:2012
Pb mg/L	0.01	IS 10500:2012
CrVI mg/L	0.05	IS 10500:2012

Table 10. BIS 10500:2012 permissible limits for the trace metals studied.

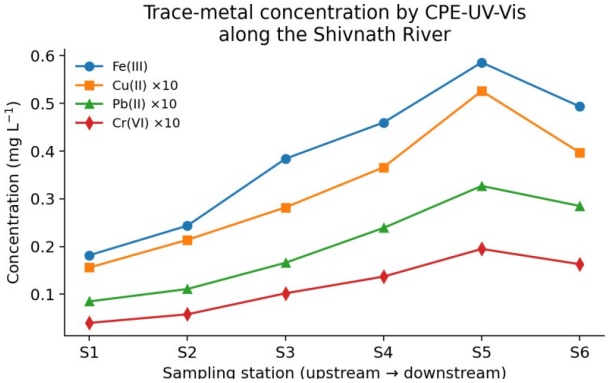

Figure 3. Station-wise trend in trace-metal concentrations along the Shivnath River (Cu, Pb and Cr(VI) scaled ×10 for visual comparability with Fe).

5.3 Composite Water Quality Index

The computed WQI (Table 11, Figure 2) increased from 50.9 (‘poor’) at the upstream station S1 to a peak of 126.2 (‘‘‘unsuitable for drinking without conventional treatment according to the adopted WQI classification’) at S5, adjacent to the Durg city barrage and water-treatment-plant intake, before declining to 114.5 at the downstream confluence station S6. This pattern is consistent with, and extends spatially, earlier WQI assessments of the Durg reach that reported a similar pre-monsoon deterioration and identified domestic and industrial wastewater discharge as the principal driver [4,5]. The result underscores the need for improved wastewater treatment coverage upstream of the S5 intake.

Station_ID	WQI	Category	Location
S1	50.85	Poor	Chhirpani (near origin), Dongargaon block, Rajnandgaon
S2	65.31	Poor	Rajnandgaon town barrage
S3	82.31	Very Poor	Mahamara Anicut, Rajnandgaon-Durg border
S4	106.1	Unfit for drinking	Rasmara Ghat, Durg district
S5	126.16	Unfit for drinking	Durg City Barrage (near Kutelabhata WTP intake)
S6	114.5	Unfit for drinking	Somnath confluence zone (Shivnath-Kharun, downstream of Durg)

Table 11. Station-wise Water Quality Index (WQI) and qualitative classification.

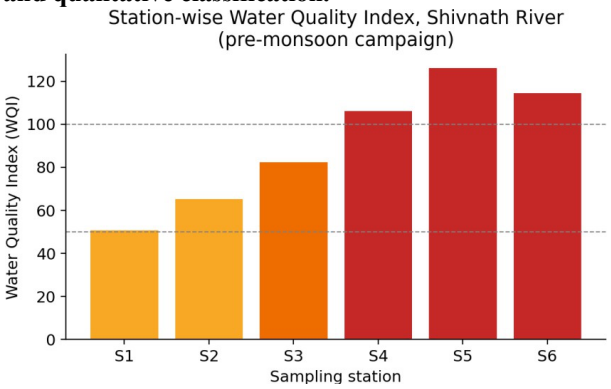

Figure 2. Station-wise Water Quality Index (WQI) along the Shivnath River; dashed lines mark the ‘good/poor’ (50) and ‘very poor/unfit’ (100) thresholds.

5.4 Correlation Among Parameters

Pearson correlation analysis of station-mean values,full matrix in the accompanying datasheet, sheet ‘Correlation_Matrix’. showed strong positive correlations ($r > 0.9$) among BOD, COD, turbidity, chloride, nitrate and all four trace metals, and a strong negative correlation between DO and this parameter group, consistent with a shared organic-pollution and urban-runoff source affecting both conventional water-quality parameters and trace-metal loading along the studied reach.

6. Conclusion

A surfactant assembly-assisted (Triton X-114 cloud point extraction) analytical protocol coupled with UV-Vis spectrophotometry was developed, optimised and validated for the determination of Fe(III), Cu(II), Pb(II) and Cr(VI) in river water, achieving 35–45-fold preconcentration, low-µg L^{-1} detection limits, recoveries of 94–102%, and results in close agreement with FAAS (≤4.0% mean bias). Applied together with standard physicochemical analysis across a six-station transect of the Shivnath River, the method revealed a consistent upstream-to-downstream deterioration in water quality, with the composite WQI shifting from ‘poor’ near the river’s upper reaches to ‘unfit for drinking without treatment’ near the Durg urban-industrial belt, accompanied by a parallel rise in trace-metal contamination, most notably Pb(II) exceeding the BIS limit from Mahamara Anicut (S3) onward.Since sampling was restricted to the pre-monsoon season, the results represent a spatial snapshot and do not capture seasonal variability.” A greenness assessment confirmed the method’s substantially reduced environmental and safety footprint relative to conventional solvent-extraction/FAAS analysis. Together, these findings demonstrate that surfactant-assembly-assisted analysis offers a practical, sustainable and cost-effective tool for routine trace-metal screening in resource-limited regional laboratories, and provide a station-resolved baseline that can inform wastewater-management priorities for the Shivnath River. Future work should extend sampling across all three hydrological seasons and multiple years, expand the analyte panel (e.g., Cd, Hg, As), and couple the CPE step with more sensitive detection (ICP-OES/MS) for ultra-trace speciation studies.

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Appendix Physiochemical datasheet

Station_ID	Replicate	pH	EC_uS_cm	TDS_mg_L	Turbidity_NTU	DO_mg_L	BOD_mg_L	COD_mg_L	Total_Hardness_mg_L	Chloride_mg_L	Nitrate_mg_L	Sulphate_mg_L	Fluoride_mg_L
S1	1	7.72	265.4	197.1	3.4	6.86	1.03	8.1	126	18	1.1	14.6	0.29
S1	2	7.63	295.8	194.4	3.1	7.74	1.05	8.4	127.7	17.8	1.2	14.9	0.28
S1	3	7.44	275.1	195.1	3.3	7.76	1.12	8.9	125.4	17.5	1.2	14.4	0.3
S2	1	7.66	325.7	220.5	4.7	7.16	1.64	12.1	149.7	26.2	2.1	19.8	0.34
S2	2	7.96	341.1	233.3	4.7	6.4	1.57	12.2	143.3	25.6	2.3	18.2	0.36
S2	3	7.05	334.3	231.9	4.7	7.15	1.66	12.3	144.6	27.1	2.1	17.8	0.32
S3	1	7.44	420.2	277	6.6	6.07	2.32	18.6	165.4	35.8	3.3	24.5	0.4
S3	2	7.33	420	268.5	6.4	6.35	2.35	18.6	167.2	34.3	3.4	22.9	0.38
S3	3	7.28	389.6	280.5	6.1	6.08	2.45	17.7	174.2	33.4	3.4	23.8	0.4
S4	1	8.23	438.5	327	8.4	5.43	2.78	24.1	185	46.5	4.6	33.5	0.47
S4	2	7.5	484.3	323.5	8.9	5.83	3.05	25.8	178.7	44.5	4.4	30.4	0.45
S4	3	8.15	474.7	296.5	7.9	5.69	3.13	26.4	217.7	47	4.4	27.7	0.49
S5	1	7.67	548.4	363.5	10.4	5.16	3.93	31.7	203.9	53.1	6	37.9	0.61

Mean Water-Quality Values Used for WQI
The three replicates were averaged before calculating the station-wise WQI.

Station	pH	DO	BOD	TDS	Hardness	Chloride	Nitrate	Turbidity
S1	7.597	7.453	1.067	195.53	126.37	17.77	1.17	3.27
S2	7.557	6.903	1.623	228.57	145.87	26.30	2.17	4.70
S3	7.350	6.167	2.373	275.33	168.93	34.50	3.37	6.37
S4	7.960	5.650	2.987	315.67	193.80	46.00	4.47	8.40
S5	7.887	4.870	3.783	363.93	209.00	58.70	6.03	10.33
S6	7.850	5.317	3.443	336.20	195.70	51.13	5.63	9.03

Quality Rating Qn Table

Station	QpH	QDO	QBOD	QTDS	QHardness	QChloride	QNitrate	QTurbidity
S1	39.78	74.44	35.56	39.11	42.12	7.11	2.59	65.33
S2	37.11	80.17	54.11	45.71	48.62	10.52	4.81	94.00
S3	23.33	87.85	79.11	55.07	56.31	13.80	7.48	127.33
S4	64.00	93.23	99.56	63.13	64.60	18.40	9.93	168.00
S5	59.11	101.35	126.11	72.79	69.67	23.48	13.41	206.67
S6	56.67	96.70	114.78	67.24	65.23	20.45	12.52	180.67

Station	WQI	Classification	Overall interpretation
S1	**50.75**	Poor	Beginning of deterioration
S2	**65.31**	Poor	Increased pollution
S3	**82.34**	Very Poor	Significant deterioration
S4	**106.05**	Unsuitable for drinking	Severe deterioration
S5	**126.19**	Unsuitable for drinking	Maximum pollution
S6	**114.57**	Unsuitable for drinking	Slight improvement but still highly degraded

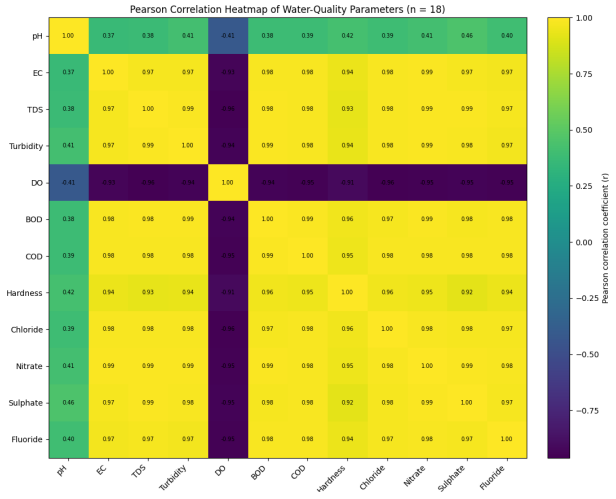
Pearson correlation coefficient r

Parameter	pH	EC	TDS	Turbidity	DO	BOD	COD	Hardness	Chloride	Nitrate	Sulphate	Fluoride
pH	1.000	0.367	0.376	0.413	-0.415	0.380	0.387	0.419	0.391	0.414	0.455	0.396
EC	0.367	1.000	**0.974**	**0.972**	**-0.935**	**0.982**	**0.984**	**0.943**	**0.980**	**0.987**	**0.969**	**0.968**
TDS	0.376	**0.974**	1.000	**0.992**	**-0.961**	**0.985**	**0.981**	**0.931**	**0.978**	**0.988**	**0.989**	**0.971**
Turbidity	0.413	**0.972**	**0.992**	1.000	**-0.945**	**0.987**	**0.977**	**0.939**	**0.978**	**0.986**	**0.984**	**0.968**

DO	-0.415	**-0.935**	**- 0.961**	**-0.945**	1.000	**-0.939**	**- 0.948**	**-0.915**	**-0.957**	**-0.949**	**-0.945**	**-0.947**
BOD	0.380	**0.982**	**0.985**	**0.987**	**-0.939**	1.000	**0.986**	**0.956**	**0.972**	**0.989**	**0.976**	**0.977**
COD	0.387	**0.984**	**0.981**	**0.977**	**-0.948**	**0.986**	1.000	**0.949**	**0.982**	**0.978**	**0.978**	**0.977**
Hardness	0.419	**0.943**	**0.931**	**0.939**	**-0.915**	**0.956**	**0.949**	1.000	**0.960**	**0.949**	**0.919**	**0.943**
Chloride	0.391	**0.980**	**0.978**	**0.978**	**-0.957**	**0.972**	**0.982**	**0.960**	1.000	**0.982**	**0.975**	**0.973**
Nitrate	0.414	**0.987**	**0.988**	**0.986**	**-0.949**	**0.989**	**0.978**	**0.949**	**0.982**	1.000	**0.986**	**0.980**
Sulphate	0.455	**0.969**	**0.989**	**0.984**	**-0.945**	**0.976**	**0.978**	**0.919**	**0.975**	**0.986**	1.000	**0.971**
Fluoride	0.396	**0.968**	**0.971**	**0.968**	**-0.947**	**0.977**	**0.977**	**0.943**	**0.973**	**0.980**	**0.971**	1.000

The p-values show that almost all correlations among the major pollution parameters are highly significant.

Correlation	r	p-value
EC–TDS	0.974	1.08×10^{-11}
EC–Turbidity	0.972	1.51×10^{-11}
EC–DO	-0.935	1.36×10^{-8}
EC–BOD	0.982	5.54×10^{-13}
EC–COD	0.984	1.76×10^{-13}
EC–Chloride	0.980	1.06×10^{-12}
EC–Nitrate	0.987	5.28×10^{-14}
TDS–Turbidity	0.992	1.21×10^{-15}
TDS–DO	-0.961	2.37×10^{-10}
TDS–BOD	0.985	1.25×10^{-13}
TDS–COD	0.981	6.78×10^{-13}
TDS–Nitrate	0.988	2.71×10^{-14}
TDS–Sulphate	0.989	1.23×10^{-14}
Turbidity–DO	-0.945	3.71×10^{-9}
Turbidity–BOD	0.987	4.99×10^{-14}
Turbidity–COD	0.977	3.50×10^{-12}
DO–BOD	-0.939	8.31×10^{-9}
DO–COD	-0.948	2.27×10^{-9}
DO–Chloride	-0.957	5.50×10^{-10}
BOD–COD	0.986	5.53×10^{-14}
BOD–Nitrate	0.989	8.50×10^{-15}
COD–Chloride	0.982	5.06×10^{-13}
Chloride–Nitrate	0.982	4.19×10^{-13}
Nitrate–Sulphate	0.986	6.45×10^{-14}


Pearson Correlation Heatmap of Water-Quality Parameters (n = 18)
pH
EC
TDS
Turbidity
DO
BOD
COD
Hardness
Chloride
Nitrate
Sulphate
Fluoride
Pearson correlation coefficient (r)
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75