Flow injection determination of anionic surfactants with cationic dyes in water bodies of central India

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A new, simple and specific flow injection analysis (FIA) procedure for the determination of anionic surfactants, *viz*., sodium lauryl sulfate (SLS), sodium dodecyl sulfonate, sodium hexadecyl sulfonate and sodium dodecyl benzenesulfonate, with cationic dyes, *viz*., Brilliant Green (BG), Malachite Green, Methylene Blue, Ethyl Violet and Crystal Violet, in water bodies, *viz*., ponds, tube wells, rivers and municipal wastes, of central India (east Madhya Pradesh) is described. It is based on the precipitation of the cationic dyes with the anionic surfactant due to formation of an ion-associate species within the pH range 5.5–8.0. The apparent molar absorptivity of the ion-associate species formed with various anionic surfactants and cationic dyes is in the range $(0.60–1.50) \times 10^4$ l mol^{-1} cm^{-1} at λ_{max} 590–665 nm. Among them, the pair BG$^+$–LS$^-$ was selected for detailed investigation. The detection limit (amount causing absorbance $> 3s$) of the method with BG is 100 ppb SLS and the sample throughput is 50 h^{-1}. Optimization of FIA and the analytical variables in the precipitation and determination of SLS with BG is described. The method is free from interferences from almost all ions which are commonly present with the surfactant. The proposed method was applied to the mapping of SLS pollution levels in the various water bodies. All surface waters and municipal waste waters and some ground waters lying near the sources were found to be contaminated with SLS beyond permissible limits.

Keywords: Flow injection analysis; spectrophotometry; cationic dyes; anionic surfactants; sodium lauryl sulfate pollution level; water bodies

Anionic surfactants have been reported as pollutants and their permissible limit in drinking water prescribed by the WHO is 1.0 ppm.[1–3] The main sources of the commonly used anionic surfactant sodium lauryl sulfate (SLS) and others, *viz*., sodium dodecyl sulfonate (SDS), sodium hexadecyl sulfonate (SHDS) and sodium dodecyl benzenesulfonate (SDBS), in water bodies are household commodities and personal care products, *e.g.*, detergents, soaps, shampoos and fabric and cosmetic materials. The level of surfactants in water bodies of densely populated countries such as India is increasing owing to the changes in lifestyle similar to western countries. Flow injection analysis (FIA) procedures for the determination of anionic surfactants based on the extraction of ion-pair species with dyes, *e.g.*, Methylene Blue and Ethyl Violet, have been reported.[4–14] Large ions (*viz*., I$^-$, IO$_3^-$, SCN$^-$, RCOO$^-$, ArO$^-$, RNH$_3^+$, R$_2$NH$_2^+$, R$_3$NH$^+$, *etc.*) form extractable ion-associate species with these dyes and interfere in the determination of anionic surfactants. In this work, a new, simple and specific FIA procedure for the determination of anionic surfactants, *viz*., SLS, SDS, SHDS and SDBS, based on precipitation of a cationic dye, *viz*., Brilliant Green (BG), is proposed. The present method is simple and reliable and overcomes most of the drawbacks of the established methods based on the extraction of the ion-associate CD$^+$–AS$^-$

(CD$^+$ = cationic dye and AS$^-$ = anionic surfactant) with comparable sensitivity.

Experimental

Apparatus

A Tecator (Höganäs, Sweden) Model 5012 flow injection analyser equipped with an ALPKEM (Wilsonville, OR, USA) Model 510 UV/VIS spectrophotometer with a 0.55 cm flow cell was employed. A Systronics Model 106 spectrophotometer with 1 cm quartz cells and a Systronics (Ahmedabad, India) Model 361 μ-pH meter were used. The FIA configuration used in this work is shown in Fig. 1.

Reagents

All chemicals were of analytical grade reagents (Merck, Darmstadt, Germany). A stock standard solution (1000 ppm or 3.5×10^{-3} mol l^{-1}) of SLS was prepared by dissolving 1.0 g of SLS in 1 l of doubly distilled water and working standard solutions were prepared by appropriate dilution of the stock standard solution. A solution of BG (0.002% m/v or 4.0×10^{-5} mol l^{-1}) was prepared by dissolving 0.010 g of BG in 0.2 ml of ethanol (95% v/v) and diluting to 500 ml with doubly distilled water. Similarly, 1000 ppm (2.8×10^{-3}–3.7×10^{-3} mol l^{-1}) solutions of other surfactants, *viz*., SDS, SHDS and SDBS, and 0.002% m/v (4.0×10^{-5}–6.3×10^{-5} mol l^{-1}) solutions of other dyes, *viz*., Malachite Green (MG), Methylene Blue (MB), Ethyl Violet (EV) and Crystal Violet (CV), were prepared. De-ionized, doubly distilled water (pH 6.0, adjusted with 0.1 mol l^{-1} acetic acid) containing 0.001% m/v (3.4×10^{-5} mol l^{-1}) potassium dichromate and 0.001% m/v (1.3×10^{-4} mol l^{-1}) thiourea was employed as the carrier. Potassium dichromate and thiourea were used to oxidize and to mask ions, *viz*., SO$_3^{2-}$ and Cu^{II}, respectively. All solutions employed were filtered and de-gassed before use.

Sample collection

Surface, ground and municipal waste water samples from central India (east Madhya Pradesh, between latitude 18 and 23° N and longitude 80°17′ and 84°11′ E) were collected in 100 ml polyethylene bottles during July and November 1997 as prescribed in the literature.[15] The sampling points for these samples were rural, urban, semi-urban and industrial areas. The
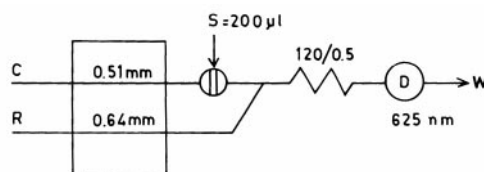
Fig. 1 Schematic diagram of FIA configuration: C = carrier, de-ionized doubly distilled water (pH 6.0, adjusted with 0.1 mol l^{-1} acetic acid) containing 0.001% m/v (3.4×10^{-5} mol l^{-1}) potassium dichromate and 0.001% m/v (1.3×10^{-4} mol l^{-1}) thiourea; R = 0.002% m/v (4.0×10^{-5} mol l^{-1}) Brilliant Green in 0.04% v/v ethanol.

samples were filtered with Whatman (Maidstone, Kent, UK) No. 42 filter-paper and stored in a refrigerator at 4 °C.

Procedure for the precipitation of the ion-associate aggregate

Five aliquots of 2.5 ml of BG (0.02% m/v or 4.0×10^{-4} mol l^{-1}) were taken in 50 ml beakers, mixed with 0, 5.0, 10.0, 15.0 and 20.0 ml of SLS (25 ppm) and diluted to 25 ml with doubly distilled water at room temperature (22 ± 2 °C). The pH was adjusted to 6.0 with dilute acetic acid (0.1 mol l^{-1}). All solutions were filtered with Whatman No. 42 filter-paper. Their absorbances were measured spectrophotometrically against a reagent blank (doubly distilled water, pH 6.0) at λ_{max} 625 nm.

Procedure for flow injection determination of anionic surfactant

For the FIA determination of anionic surfactants, two silicon tubes of bore size 0.51 and 0.64 mm to propel doubly distilled water and dye solution, respectively, were used. A smooth baseline having zero absorbance was plotted under the optimum FIA conditions (Fig. 1). A 200 µl aliquot of the analyte solution containing up to 20.0 ppm SLS (or 7.0×10^{-5} mol l^{-1} anionic surfactant) was injected. The decrease in colour of the flowing stream was plotted at λ_{max}. The filtered water sample was injected in the same way. The concentration of the anionic surfactant in terms of SLS in the sample was determined from the calibration curve obtained.

Results and discussion

Precipitation and composition of ion-associate species

The cationic dyes BG, MG, MB, EV and CV form an ion-associate precipitate with the anionic surfactants SLS, SDS, SHDS and SDBS when they are present at higher concentration levels in the aqueous solution.[16,17] The colour intensity decreases quantitatively when the anionic surfactant SLS is added within the pH range 5.5–8.0 owing to formation of a slightly soluble ion-associate species (Fig. 2). The decrease in colour of the dye was found to be linear up to 20 ppm SLS with a slope, intercept and correlation coefficient of −0.028, 0.988 and 0.999, respectively.

Their stoichiometry was determined by the FIA technique using the curve-fitting method, plotting log $(h_{eq}/h_{max} - h_{eq})$ *versus* log (molar concentration of SLS injected). The results indicated that the cationic dye (CD⁺) reacted with the anionic surfactant (AS⁻) in 1 : 1 molar ratio. The decrease in colour of
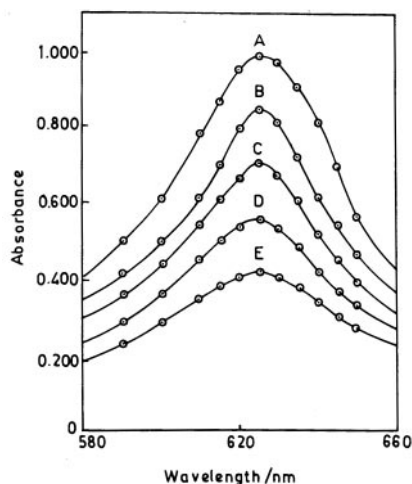
the dye is due to precipitation of the ion-associate species, CD⁺–AS⁻, in a similar fashion as described in the literature.[16,17]

Optimization of analytical variables

A dilute acetic acid solution (0.1 mol l^{-1}) was employed to maintain the pH of the carrier (C). The optimum acidity range for the determination of SLS was found to be in the pH range 5.5–8.0, hence further experimental work was carried out at pH 6.0. Similarly, the optimum pH range of the sample solutions injected is 6.0–8.0. Potassium dichromate and thiourea were used in the carrier to enhance the tolerance limits of diverse ions, *viz.*, SO_3^{2-} and Cu^{II}, by oxidizing and masking them, respectively. An increase in concentration of BG up to 0.004% m/v (8.0×10^{-5} mol l^{-1}) enhanced the peak height but a 0.002% m/v (4.0×10^{-5} mol l^{-1}) solution was used for detailed studies as no smooth baseline was recorded beyond this concentration. The use of an alcohol, *viz.*, ethanol, enhanced the peak height with a smoother baseline owing to the higher solubility. A 0.04% v/v concentration of ethanol in the dye solution was found to be adequate for the determination of the surfactant. The effect of temperature on the peak height was examined and a maximum and constant peak height was obtained when the coil was dipped into a water-bath maintained between 15 and 40 °C. The effect of the nature of dye and of the surfactant on the peak height was examined. The replacement of BG in the ion-associate species with other dyes, *viz.*, MG, MB, EV and CV, decreased the sensitivity of the reaction considerably owing either to a lower +I effect (MG), lower conjugation (MB) or greater steric hindrance (EV, CV). In the case of surfactants, the sensitivity of the reaction increased as the molecular mass of the surfactants increased from SDS to SDBS (Fig. 3), which may be due to an increase in either the −I effect or the carbon chain, or both. Among them, the pair BG⁺–LS⁻ was selected for detailed investigation.

Optimization of FIA variables

The effect of FIA variables, *viz.*, bore size of silicon tubes, length of reaction coils, volume size of the solution injected and residence time, on the peak height were examined. The optimum bore size of the silicon tubes used is shown in Fig. 1. A PTFE tube of bore size 0.5 mm was used throughout the work. The peak height increased with increase in the reaction coil length up to 180 cm but after 120 cm no smooth baseline was recorded. A constant and maximum peak height was recorded over the volume range 200–370 µl. Injection and residence times of at least 25 and 45 s, respectively, were found to be adequate to obtain a maximum and constant peak height

Fig. 2 Absorption spectra of Brilliant Green in sodium lauryl sulfate solutions. BG, 0.002% m/v (4.0×10^{-5} mol l^{-1}) in 0.04% v/v ethanol; concentration of SLS: A, 0; B, 5; C, 10; D, 15; E, 20 ppm.
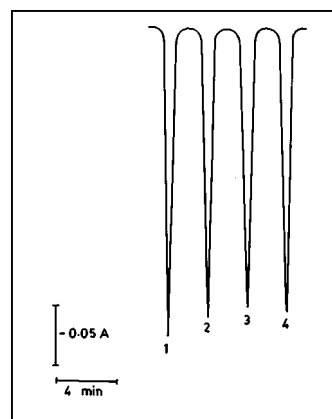
Fig. 3 Signals of various surfactants with brilliant green. 1 = sodium laurylsulfate (SLS), 2 = sodium dodecylsulfonate (SDS), 3 = sodium hexadecylsulfonate (SHDS), 4 = sodium dodecylbenzenesulfonate (SDBS).

with better resolution. Silicon tubes of bore size 0.51 and 0.64 mm, a PTFE coil of size 120 cm $\times$ 0.5 mm and a volume of sample solution of 200 µl were selected for detailed investigation. The sample throughput was determined and found to be 50 h^{-1} at a flow rate of 1.6 ml min^{-1}.

Optimum concentration range, detection limit, sensitivity and statistics

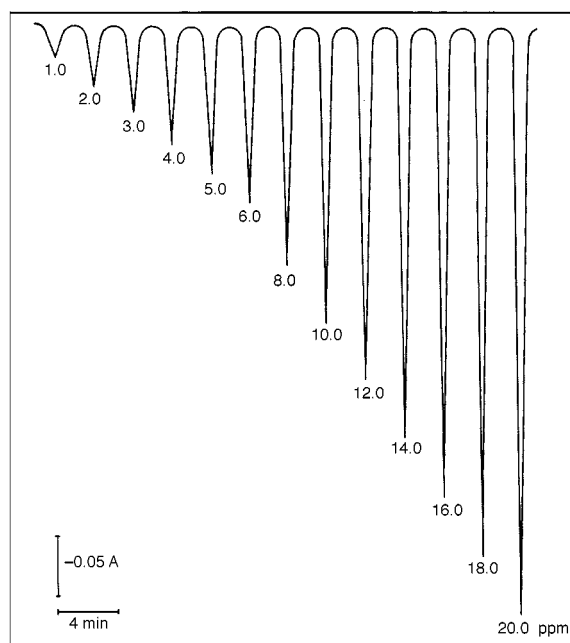The anionic surfactant SLS was used as a representative surfactant and a calibration curve was obtained using standard solutions of SLS. The curve was linear up to 20.0 ppm of SLS at a gain factor of 1 with a slope, intercept and correlation coefficient of -1.0, 0.005 and 0.999, respectively (Fig. 4). The apparent molar absorptivity of the ion-associate precipitate formed (calculated using the molar concentration of surfactant injected and a pathlength of the flow cell of 0.55 cm) with five dyes and four anionic surfactants was found to be in the range of $(0.60–1.50) \times 10^4$ l mol^{-1} cm^{-1} at the absorption maximum,

Fig. 4 Signal peak height recorded for standard solution of SLS, 1.0–20.0 ppm.

Table 1 Effect of various dyes and surfactants on the absorptivity

Surfactant	Dye	λ_{max}/ nm	Apparent ε/ 10^4 l mol^{-1} cm^{-1}
SLS [$CH_3(CH_2)_{11}OSO_3Na$]	BG	625	1.30
	MG	630	0.60
	MB	665	0.90
	EV	595	0.70
	CV	590	0.60
SDS [$CH_3(CH_2)_{11}SO_3Na$]	BG	625	1.20
SHDS [$CH_3(CH_2)_{15} SO_3Na$]	BG	625	1.40
SDBS [$CH_3(CH_2)_{11}C_6H_4SO_3Na$]	BG	625	1.50

Table 2 Effect of diverse ions on the determination of 5.0 ppm of SLS

Ions added	Tolerance limit* (ppm)
Na, K, SCN$^-$, S^{2-}, I$^-$	500
NO$_3^-$	400
SO$_4^{2-}$	250
Br$^-$, Ca^{II}	200
Cl$^-$, Mg^{II}, TX-100, TX-300, Briz-35	100
Al^{III}, Ni^{II}, Mn^{II}, Co^{II}	50
Fe^{III}, PO$_4^{3-}$	25
F$^-$, V^V, Cr^{VI}, Zn^{II}, thiourea	20
Bi^{III}, Cu^{II}, CPC, CTAB, SO$_3^{2-}$	10

* Causing an error $< \pm 2\%$.

Table 3 Comparison of the present method with Methylene Blue methods[5,18] for samples collected during November 1997

Sampling point	Present method		FIA method[5]		Manual method[18]	
	SLS found (ppm)	RSD* (%)	SLS found (ppm)	RSD* (%)	SLS found (ppm)	RSD* (%)
Ponds—						
Budha	13.8	0.5	14.2	1.3	12.7	1.0
Kankali	12.6	0.5	13.5	1.4		
Raja	21.8	0.6	23.2	1.2		
Katora	18.1	0.5	18.9	1.2		
Handi	12.0	0.6	12.5	1.3		
Rivers—						
Kharoon	1.3	0.8	1.7	1.6	2.6	1.1
Hasdo	3.0	0.7	3.6	1.7		
Shivnath	2.2	0.7	2.8	1.6		
Arpa	2.8	0.6	3.4	1.8		
Ground waters—						
Budhapara	2.8	0.7	2.0	2.0	1.5	1.3
Kankalipara	2.2	0.8	2.4	1.9		
Raja talab	4.2	0.6	4.5	1.8		
Katora talab	3.5	0.7	3.8	1.6		
Handipara	4.6	0.6	5.3	1.5		
Municipal waste waters—						
Raipur	34.4	0.5	36.0	1.4	32.0	1.0
Bhilai	42.2	0.4	43.8	1.2		
Durg	32.0	0.5	33.2	1.2		
Rajnandgaon	25.6	0.6	27.0	1.3		
Raigarh	23.2	0.6	25.8	1.3		
Bilaspur	29.3	0.5	32.0	1.4		

* Six replicate measurements were made.

590–665 nm (Table 1). The detection limit (the amount causing an absorbance or peak height more than three times the standard deviation of the blank) was determined and found to be 100 ppb SLS with BG. The relative standard deviation for the determination of 10.0 ppm of SLS ($n = 6$) was found to be 0.5%.

Effect of diverse ions

The effect of various diverse ions on the determination of 5.0 ppm of SLS was examined using the proposed procedure. Only the tolerance limit of the ions Cu^{II} and SO_3^{2-} was found to be critical, but it could be increased by adding potassium dichromate (0.001% m/v or 3.4×10^{-5} mol l^{-1}) and thiourea

(0.001% m/v or 1.3×10^{-4} mol l^{-1}) solutions, respectively, to the carrier. Cationic surfactants, *viz.*, cetylpyridinium chloride (CPC) and cetyltrimethylammonium bromide (CTAB), could be tolerated up to at least a twofold mass excess and thereafter they caused a positive effect (decrease peak height). The tolerance limits of various diverse ions tested in the determination of 5.0 ppm of SLS are summarized in Table 2.

Application of the method

The validity of the method was checked with the conventional manual and FIA Methylene Blue methods[5,18] and its precision was found to be better than those of the established methods (Table 3). The application of the present method to the determination of anionic surfactants in terms of SLS was extended to various water bodies, *viz.*, 53 ponds, 11 rivers, 53 tube wells and six municipal waste waters from central India (see Experimental). All pond, river and municipal waste waters were found to be contaminated with SLS in the ranges 6.0–22.6 (mean 13.6, median 13.2, standard deviation 4.3), 1.0–3.0 (mean 1.9, median 1.8, standard deviation 0.6), and 23.2–42.2 (mean 31.1, median 30.6, standard deviation 6.8) ppm, respectively (Tables 4–6). In addition, the shallow tube well waters lying near stationary surface and municipal waste water reservoirs were also found to be contaminated with SLS in the range of 1.2–4.6 (mean 2.6, median 2.5, standard deviation 0.8) ppm (Table 7). The highest level of the surfactant of up to 42.2 ppm of SLS was observed in municipal waste water and the lowest level of down to 1.0 ppm SLS in the mobile surface and ground waters. The level of SLS in the pond water decreased by approximately half in the rainy season whereas it increased at least threefold in the tube well ground water (Table 8). The high values of the standard deviation for the SLS level in the pond water (4.3 ppm) and municipal waste water (6.8 ppm) show that the nature and strength of the primary anthropogenic sources, *viz.*, use of detergents, soaps, shampoos, cosmetics, *etc.*, and meteorological, geographical and geological factors differ from

Table 4 Determination of SLS in stationary surface waters collected during November 1997

Sampling point (ponds)	Place	SLS found (ppm)*
Budha	Raipur	13.8
Kankali		12.6
Raja		21.8
Katora		18.1
Handi		12.0
Bendri		10.7
Guma		7.6
Tandua		6.0
Kukurbeda		10.2
Labhandi		9.4
Chherikhedi		8.0
Kota		16.2
Jora		9.2
Dharampura		7.8
Lalpur		7.5
Mandir Hasaud		8.4
Kalyansagar, Bhatapara		13.2
Baloda Bazar		12.5
Arang		16.1
Mahasamund		11.7
Dhamtari		17.3
Kumhari	Durg	18.4
Charoda		14.2
Borsi		19.4
Kugda		17.6
Suryakund, Bhilai		13.5
Nehru Nagar		15.0
Luchki		20.2
Hudco		22.6
Sarkanda	Bilaspur	17.4
Juna Bilaspur		19.5
Ratanpur		11.5
Bheema, Janjgir		14.3
Sardha, Lormi		8.3
Lormi		11.4
Mungeli		10.3
Pandaria		9.2
Panchavati		15.0
Torva Naka		18.2
Chandrapur		12.7
Korba		19.3
Champa		16.2
Dalpatsagar	Bastar	18.8
Bhanupratappur		10.4
Narayanpur		11.5
Kanker		12.4
Keshkal		10.3
Bal Samund	Raigarh	10.2
Mithumuda		18.5
Tarapur		6.9
Sarangarh		14.0
Rajnandgaon	Rajnandgaon	18.3
Chichola		16.2

* Mean 13.6, median 13.2, range 6.0–22.6, SD 4.3 ppm.

Table 5 Determination of SLS in river waters collected during November 1997

Sampling point (rivers)	Place	SLS found (ppm)*
Kharoon	Raipur	1.3
Shivnath	Durg	2.2
Hasdo, Korba	Bilaspur	3.0
Hasdo, Champa		2.4
Mahanadi, Sheorinarayan		1.0
Arpa		2.8
Kelo	Raigarh	1.8
Mand		1.2
Indravati	Bastar	1.7
Dudh, Kanker		2.1
Maitrayani	Rajnandgaon	1.5

* Mean 1.9, median 1.8, range 1.0–3.0, SD 0.6 ppm.

Table 6 Determination of SLS in municipal waste waters during November 1997

Sampling point	Place	SLS found (ppm)*
Raipur	Raipur	34.4
Bhilai	Durg	42.2
Durg		32.0
Rajnandgaon	Rajnandgaon	25.6
Raigarh	Raigarh	23.2
Bilaspur	Bilaspur	29.3

* Mean 31.1, median 30.6, range 23.2–42.2, SD 6.8 ppm.

Table 7 Determination of SLS in ground waters collected during November 1997

Sampling point (tube wells)	Place	SLS found (ppm)*
Budhapara	Raipur	2.8
Kankalipara		2.2
Raja talab		4.2
Katora talab		3.5
Handipara		4.6
Bendri		2.5
Guma		1.2
Tendua		1.4
Kukurbeda		2.0
Labhandi		1.8
Chherikhedi		1.6
Kota		3.2
Jora		1.7
Dharampura		2.1
Lalpur		2.4
Mandir Hasaud		2.7
Kalyansagar, Bhatapara		3.1
Baloda Bazar		2.4
Arang		1.9
Mahasamund		2.6
Dhamtari		2.8
Kumhari	Durg	3.9
Charoda		2.6
Borsi		1.7
Kugda		2.2
Suryakund, Bhilai		2.5
Nehru Nagar		2.2
Luchki		3.5
Hudco		2.4
Sarkanda	Bilaspur	3.7
Juna Bilaspur		2.8
Ratanpur		3.1
Bheema, Janjgir		3.8
Sardha, Lormi		1.8
Lormi		2.3
Mungeli		2.5
Pandaria		2.0
Panchavati		3.2
Torva Naka		2.2
Chandrapur		1.8
Korba		4.5
Champa		3.5
Dalpatsagar	Bastar	4.2
Bhanuprattappur		2.2
Narayanpur		2.8
Kanker		2.4
Keshkal		2.4
Bal Samund	Raigarh	2.2
Mithumuda		3.2
Tarapur		1.8
Sarangarh		2.8
Rajnandgaon	Rajnandgaon	3.5
Chichola		2.1

* Mean 2.6, median 2.5, range 1.2–4.6, SD 0.8 ppm.

Table 8 Seasonal variation of SLS levels in various water bodies (location, Raipur)

Sampling point	Date of collection	SLS found (ppm)
Raja pond	21 July 1997	11.8
Raja pond	15 November 1997	21.8
Raja tubewell	22 July 1997	11.2
Raja tubewell	15 November 1997	4.2

Conclusion

Proposed method is simple, specific and precise and is applicable to the determination of anionic surfactants in terms of SLS in various water bodies of central India. Almost all the surface waters of rural, urban, semi-urban and industrial areas and shallow tube well waters lying near the sources were found to be contaminated with SLS beyond the permissible limit (>1.0 ppm). The main sources of anionic surfactants in water bodies of central India are assumed to be household commodities and personal care products, *viz.*, detergents, soaps and fabric and cosmetic materials, *etc.*

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place to place in central India. The lower standard deviations for river water (0.6 ppm) and tube well water (0.8 ppm) water show that they will be polluted by secondary sources, *viz.*, polluted ponds, municipal waste water reservoirs, *etc.*