

Supplementary materials

**KBr-impregnated paper substrate as sample probe for enhanced
ATR-FTIR signal strength of anionic and non-ionic surfactants in
aqueous medium**

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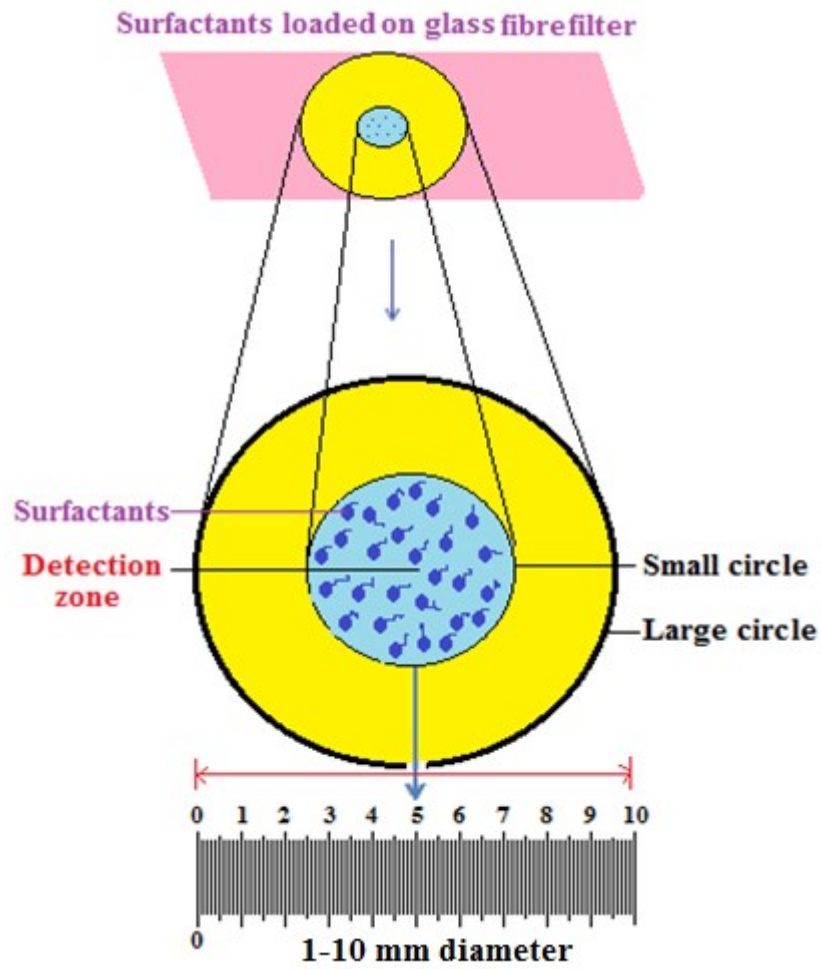


Fig. S1. The testing sheet consisting 5 mm diameter hydrophilic area for samples pre-concentration

SEM-EDX analysis

The micro-structure and elemental composition of paper before and after addition of AS and NS were confirmed using SEM-EDX as depicted in Fig. S2 (a-b). After air-dried, the samples were passed through a 0.65 micrometer of filter paper. Then, samples were mounted on stubs with conductive carbon tape and coated with carbon.¹ All samples were analyzed for their micro-structure and elemental compositions under JEOL JSM-6701F FE-SEM operating at 15 kV. The surface morphology of GFF paper was observed to be smooth and regular with fewer undulations after the AS and NS were subjected to adsorption process at various magnifications ranging from X3000-5000. EDX spectrum shows the presence of oxygen (O), silicon (Si), carbon (C), magnesium (Mg), sodium (Na), barium (Ba), aluminium (Al), sulphur (S), potassium (K), Bromide (Br) and calcium (Ca). The weight percentage (wt %) of all elements before AS and NS adsorption is investigated in the following order: O (60.30%) > Si (39.97%) > Br (32.07%) > C (10.03%). Similarly, the wt% of all elements present in GFF after adsorption was investigated as following order: O (60.01%) > Si (30.35%) > Mg (15.00%) > Na (10.21%) > Ba (8.54%) > Al (8.14%) > S (7.02%) > K (5.85%) > Br (4.93%) > Ca (5.02%), shown in Fig. S2 (a-b). It is apparent in the inserted part of Fig. S2(a) that oxygen (O) and silicon (Si) atom is dominant in the component, and there are trace amounts of carbon (C) atom present in the GFF, which is similar to that of after deposition AS and NS on KBr-impregnated paper substrate (Fig. S2(b)). This approach confirmed the adsorption of AS and NS on the surface of paper substrate and the interaction of silicate (SiO₄) containing KBr-impregnated paper surface with analytes.

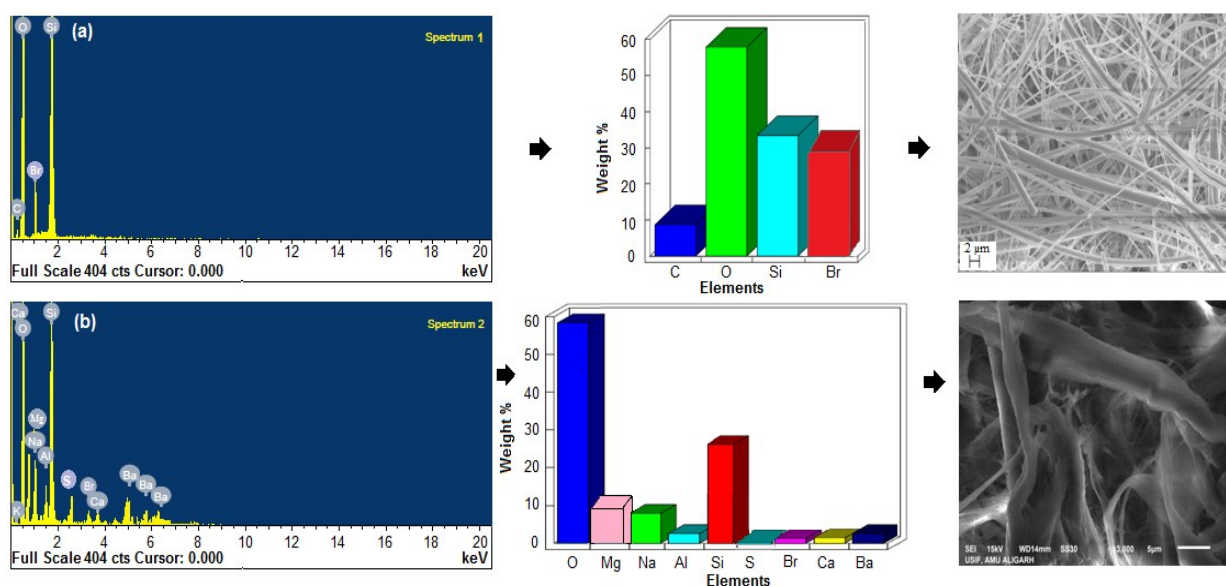


Fig. S2. SEM-EDX analysis of KBr-impregnated paper substrate before adsorption (a); and after adsorption (b) of mixed AS and NS at the magnification of X3000.

Physical phenomenon for effective adsorption of surfactants onto GFF paper substrate

Based on physical phenomenon, the reason for enhancement of IR signal is that the crystal must have a higher refractive index than the specimen. It is to be noted that mixed AS and NS strongly adsorbed on paper in the wavelength range of 4000-900 cm^{-1} . The paper substrate served to increase IR signals of mixed AS and NS due to the higher interaction of evanescent wave of the reflected radiation with KBr-impregnated paper surface. The adsorption (penetration depth 0.5 micron to several microns) of AS and NS onto the paper substrate contributes an additional signal enhancement when the infra-red light directly contacts with the AS and NS loaded on paper substrate. The incident IR radiation penetrates into the sample depending on wavelength and refraction indices of both ATR element as well as sample-penetration depth with not more than a few microns, Ventura-Gayetea et al. 2004.² Thus, ATR spectra shows the information of smooth surface of paper substrate. Further, since the density and pathlength of KBr substrate, which are directly proportional to the intensity of IR radiation, ultimately reflect to the variations in the analytical results, we have measured the standard deviation and other statistical parameters towards accuracy and precision of the results with great acceptability. The methods described here can also be used for detecting the presence of water in a sample. It is largely undesirable to have water in a sample being analyzed using FTIR with ATR accessories based methods as water can affect the accuracy of quantification of AS and NS. In a representative experiment, 20 μL of a 100 $\mu\text{g L}^{-1}$ mixed AS and NS solution in ultrapure water was directly placed within the ZnSe crystal for measurement of ATR-FTIR spectrometer. A broad absorption band due to the presence of H_2O is always observed. Actually, aqueous solutions can have a problem of uniform drying and obtaining a uniform distribution of analytes on the detection zone of the crystal being exposed to an IR signal.³

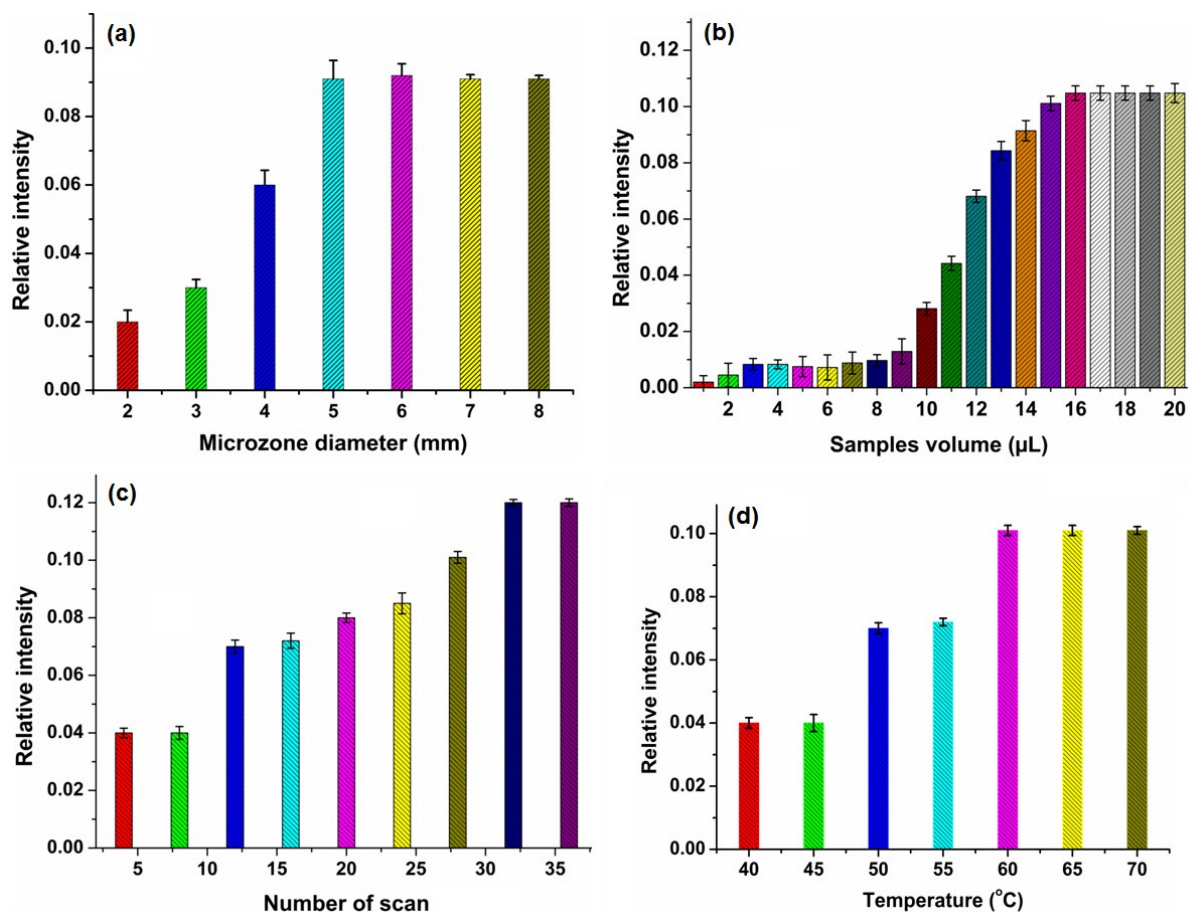


Fig. S3. Experimental optimization: effect of microzone diameter ($C_{AS, NS} (10 \mu\text{gL}^{-1}) = 20 \mu\text{L}$; sample volume= $20 \mu\text{L}$; number of scan =15; temperature= 65°C for 2 min) (a), effect of sample volume (paper diameter = 5mm; number of scan =15; temperature= 65°C for 2 min) (b), number of scan ($C_{AS, NS} (10 \mu\text{gL}^{-1}) = 20 \mu\text{L}$; paper diameter =5mm; sample volume= $20 \mu\text{L}$; temperature = 65°C for 2 min) (c) and effect of temperature ($C_{AS, NS} (10 \mu\text{gL}^{-1}) = 20 \mu\text{L}$; paper diameter =5mm; sample volume= $20 \mu\text{L}$; number of scan =15) (d) for the determination of AS and NS using KBr-impregnated paper substrate.

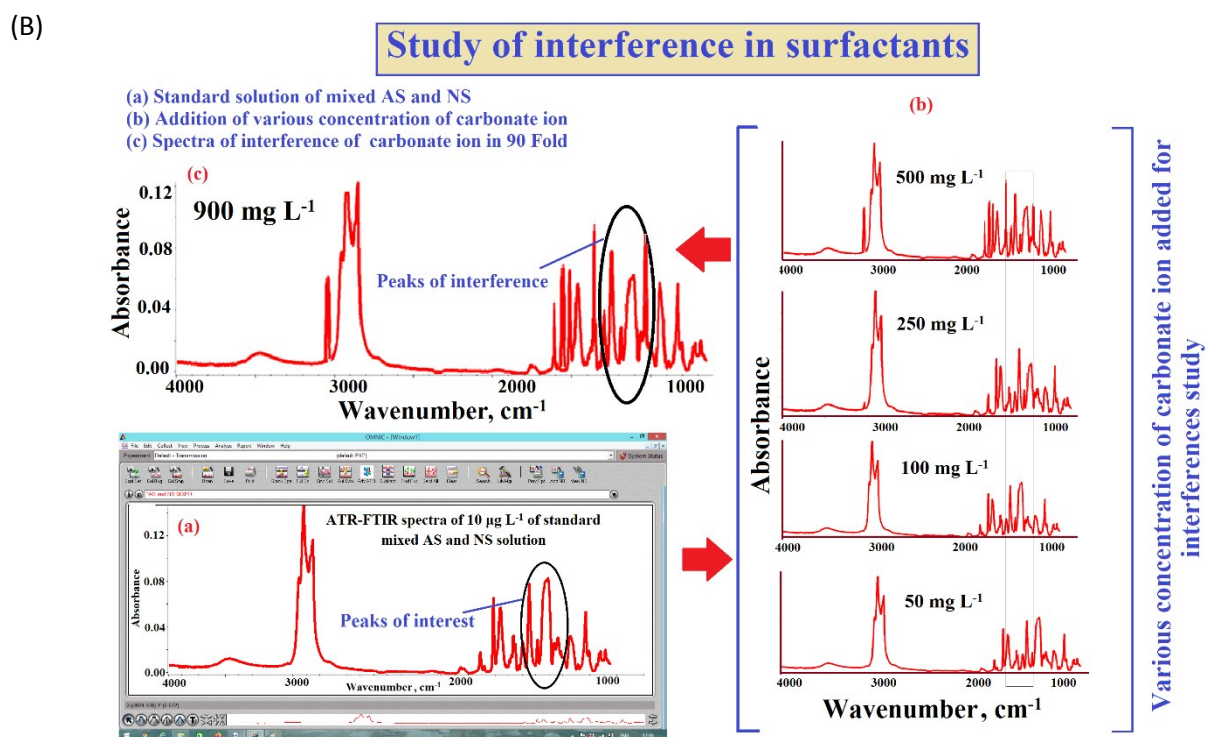
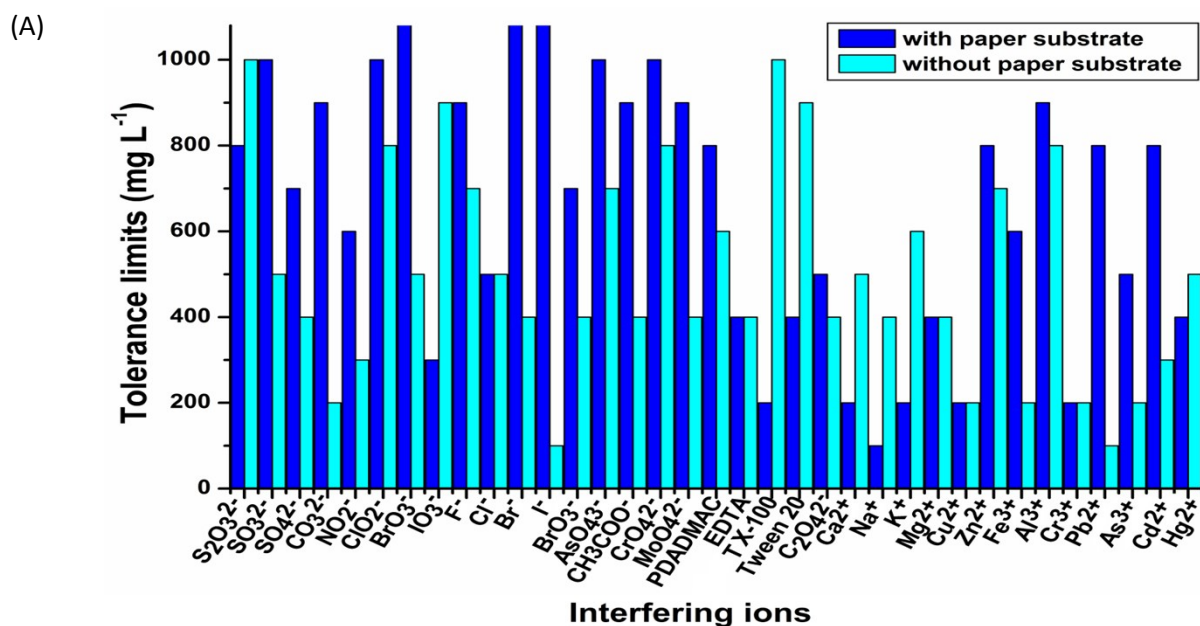


Fig. S4. (A) The tolerance limits of different metal ions, anions and polycation due to the test of interferences for selective determination of AS and NS with and without using paper substrate and (B) interferences on mixed AS and NS using KBr-impregnated paper coupled with ATR-FTIR ($C_{AS, NS}$ ($10 \mu\text{g L}^{-1}$) = $20 \mu\text{L}$; paper diameter = 5mm; number of scan = 15; temperature = 65°C for 2 min; interfering ions e.g., carbonate ($50\text{--}1000 \text{ mg L}^{-1}$) = $20 \mu\text{L}$).

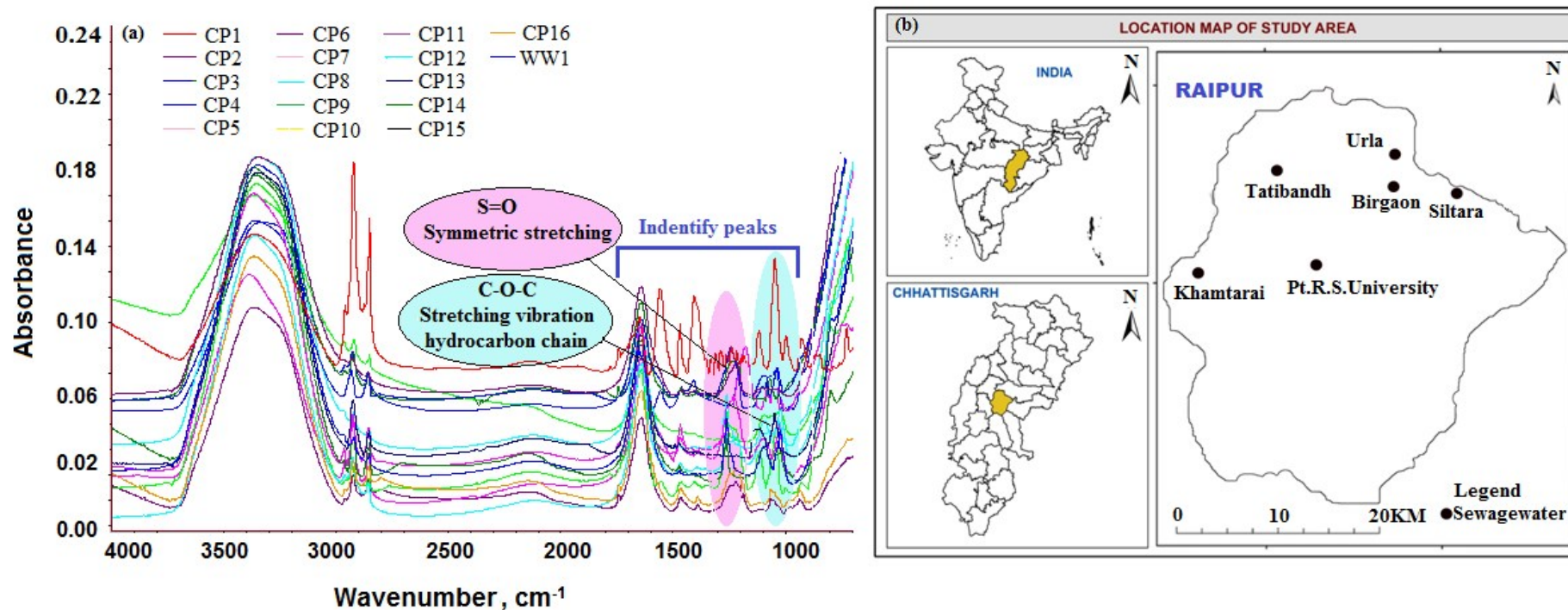


Fig. S5. ATR-FTIR spectra of various commodity samples using KBr-impregnated paper (a) and location map of study area for wastewater sampling (b): (commodity and water sample = 20 μL ; paper diameter = 5mm; number of scan =15; temperature = 65°C for 2 min).

Table S1. Optimum instrumental condition for determination of total mixed AS and NS using KBr-impregnated GFF substrate.

Particulars	Descriptions
Instrument	Fourier-transform infrared spectrometer, Nicolet iS10, Thermo Fisher Scientific Instrument, Madison, USA
Technique	Attenuated total reflectance spectroscopy
Software	Omnic 9 TQ analysis
Beam splitter	KBr
Detector	Deuterated, L-alanine doped triglycine sulfate (DLATGS)
Measurement mode	Absorbance
Resolution	4 cm ⁻¹
No. of scanning	15
Sample volume	20 μL
Substrate	Glass fiber filter (GFF)
Sample form	Wet-state to dry-state

Table S2. Infrared absorption bands and different modes of vibrations for AS and NS before and after deposition over KBr-impregnated GFF substrate $C_{AS, NS} (100 \mu\text{gL}^{-1}) = 20 \mu\text{L}$; paper diameter = 5mm; number of scan =15; temperature = 65°C for 2 min).

Surfactants	Group	Peak assignment	Present method		Reported spectral data of pure compound Peak (cm^{-1})
			Without KBr-impregnated paper substrate Peak (cm^{-1})	With KBr-impregnated paper substrate Peak (cm^{-1})	
AS	Methylene chain	CH_3 Asymmetric stretching	2972-2950	2919-2960	2955-2950
	Methylene chain	CH_3 Symmetric stretching	2853-2870	2853-2850	2873-2870
	Alkyl chain	CH_2 Stretching Vibration	2919-2900	2919-2900	2917-2901
	Sulfate	$\text{S}=\text{O}$ Symmetric stretching	1226-1200	1226-1200	1249-1200
	Aromatic hydrocarbon chain	CH_2 Bending vibration	1660-1500	1616-1500	1511-1500
	Terminal Methylene	CH_2 Wagging vibration	1466-1450	1466-1400	1470-1450
	Aromatic	Ar-O- CH_2 vibration	989-850	989-850	950-800
NS	Alkyl chain	C-H Asymmetric stretching	2954-2800	2981-2954	2880-2800
	Alkyl chain	C-H Symmetric stretching	2874-2880	2874-2800	2880-2840
	Aromatic	Ar-O- CH_2 vibration	1519-1500	1519-1500	1511-1500
	Terminal Methylene	CH_2 Wagging vibration	1466-1450	1457-1450	1470-1450
	Acyl chain	$\text{C}=\text{C}$ Stretching vibration	1250-1300	1350-1250	1360-1300
	Aromatic hydrocarbon chain	C-O-C Stretching vibration	1110-1050	1110-1050	1110-1050
	Mixed AS and NS	Alkyl chain	C-H Asymmetric stretching	2954-2900	2981-2900
Alkyl chain		C-H Symmetric stretching	2874-2800	2874-2800	ND
Terminal Methylene		CH_2 Wagging vibration	1466-1450	1472-1466	
Aromatic hydrocarbon chain		C-O-C Stretching vibration	1110-1050	1114-1050	ND
Sulfate		$\text{S}=\text{O}$ Symmetric stretching	1237-1200	1253-1200	ND

Table S3. Assay validation parameters for determination of AS and NS using KBr-impregnated paper coupled with ATR-FTIR spectroscopy.

KBr-impregnated paper/ATR-FTIR		MWCNT /Potentiometric titrations	
(Present method)		(Reference Method)	
Parameters	Results	Parameters	Results
Linearity ($\mu\text{g L}^{-1}$)	10-100	Linearity (mmol L^{-1})	2.5×10^{-8} - 1.9×10^{-3}
Accuracy (mean \pm S.D)	0.167 ± 0.008	Accuracy (mean \pm S.D)	0.03-1.8
Precision (RSD %)	5.5	Precision (RSD %)	1.8
Intermediate precision	3.2	Intermediate precision	ND
Slope	0.049	Slope	57.1 ± 1.1
Intercept	0.003	Intercept	-41.4 ± 4.9
Correlation estimation (R)	0.994, 0.997	Correlation estimation	0.995
Correlation coefficient (R^2)	0.989, 0.994	Correlation coefficient (R)	0.998
MDL($\mu\text{g L}^{-1}$)	4.0	MDL(mmol L^{-1})	1.2×10^{-7}
MQL ($\mu\text{g L}^{-1}$)	12.0	MQL (mmol L^{-1})	ND
Robustness (mean \pm S.D)	0.008	Robustness (mean \pm S.D)	ND
Concentration ranged ($\mu\text{g L}^{-1}$)	0.01-8.01	Concentration ranged (mmol L^{-1})	2.0×10^{-7} - 1.1×10^{-3}
Trueness (%)	1.5-4.1	Trueness (%)	ND
Matrix effect ($\mu\text{g L}^{-1}$)	0.05-24.6, 19.3-75.1	Matrix effect	ND
Recovery (%)	71.4-109.7	Recovery (%)	99.1-102.6
F-Test (95 % confidence limit)	1.5-5.4	F-Test (95 % confidence limit)	ND
<i>t</i> - Test (95 % confidence limit)	1.0-2.4	<i>t</i> - Test (95 % confidence limit)	ND

ND=not detected, MWCNT=multi-walled carbon nanotubes

Reference

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2. J.F. Ventura-Gayete, B.F. Reis, S. Garrigues, A. Morales-Rubio and M.de la Guardia, *Microchemical Journal*, 2004, **78**(1), 47-54.
3. D. Bach and I.R. Miller, *Biochimica et. Biophysica Acta*. 2001, **1514**, 318-326.