

Analytical Role of Sodium Dodecyl Sulphate in ICP-AES

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Summary: Effect of Sodium Dodecyl Sulphate (SDS) on sample transport efficiency, nebulisation and overall contribution in analysis using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for different analytes has been studied. The objective of this study was to investigate the effect of surfactant on the quality of aerosols results in enhancement or depression of the final analyte signals. The SDS is anionic in nature, has been added to set of standards containing Cr, Fe, Co, Ni, Cu, Cd and Pb in the presence of 0.01% - 2.0% HNO₃. Typical property of surfactants i.e. lowering of surface tension has been exploited to modify the analytical procedures for analysis through ICP-AES. Determinations were carried out using 5 ppm analytes under a set of conditions i.e. below Critical Micelle Concentration (CMC) at CMC and above CMC of the surfactant used. All glass Meinhard pneumatic nebuliser was used for the nebulisation processes. The results have been explained on the basis of a mild action of the surfactants to modify the plasma analytical conditions due to the change in the overall physical parameters.

Key words: SDS; HNO₃; ICP-AES; metal determinations.

Introduction

The most common mean of sample introduction in ICP-AES involves pneumatic generation of aerosols [1, 2]. Several studies are available in literature, describe the aerosols for sample introduction and examine the relationships between the aerosol properties and analytical performance [3-5]. In general, the effect of high acid concentrations has been described by many workers, which might be used during the sample digestion and preparation. On the other hand some accuracy problems at low acid concentration level have been also reported [6].

Determinations of analytes using ICP-AES have been investigated under the influence of particular surfactants and acids concentrations [4-7]. Other workers [8, 9] have also studied the subject especially where surface tension was varied by the addition of particular surfactants to sample solutions, but no cohesive model has yet been developed at low-level analyte concentration. The emission enhancement or depression of the signal, apart from other factors, has been attributed to the uptake rate because of variation in surface tension, density and viscosity, with overall nebuliser efficiency and thus droplet size distribution [10, 11].

Many researchers have suggested the use of surfactants to enhance the sample transport process by lowering surface tension along with low acids concentrations [12-14]. However some authors have also investigated changes in the plasma excitation conditions as dependent upon the element selection

and type of the generators used [13-16]. Pharr [17] investigated that the micellar systems for metal ions using different cations and the anions to explain the enhancement of the intensity of the analyte in the presence of Sodium dodecyl sulphate (SDS).

In the present work, Sodium Dodecyl Sulphate; anionic surfactant is used to observe the ICP-AES performance for seven analytes in the presence of HNO₃. Signal intensities of analytes have been investigated using a set of three concentrations of SDS and with a low acid concentration range for each concentration of SDS. A model is proposed here in Fig. 4 to describe the transportation mechanism of metal ions under the influence of anionic surfactant, which may be explained on the basis of expected migration of surfactant ions to the interface, formation of micelles and then reorientation of micelles. The model also describes the stripping action, splitting of droplets and enrichment of smaller droplets formed to accommodate the analytes.

Results and Discussion

Effect of HNO₃, SDS and HNO₃ plus SDS on the analytes i.e. Cr, Fe, Co, Ni, Cu, Cd and Pb studied have been shown in Fig. 1, Fig. 2 and Fig. 3 respectively. All the results depicted have been discussed in detail after the following points.

- a) Fig.1 shows the relative intensities of the analytes under the influence of HNO₃ concentration range, which was used during all the observations. HNO₃ more or less

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shows both enhancement and suppression at different conc. for each particular analyte. Signal intensity is observed to be dependent on the acid concentrations and the overall depression of signals was observed at higher acid concentrations while some reduction at some low acidity is also investigated.

- b) At micellar (10mM) SDS concentration, enhancement of the signal has been noticed at low HNO₃ concentrations studied. The enhancement effect decreases as the acid concentration is increased. This pattern seems to be uniform for all the analytes but different for Pb where intensity suppressed at low acid concentration and then increased with the increase in acidity.
- c) At post micellar (50mM) higher than CMC (10mM) conc. of SDS, the enhancement of the signal intensity slightly decreased as compared to the micellar phase. Thus approaches approximately near to the intensity of blank. The acid approximately showed the same trend i.e. the intensity decreases with the increase of acidity. This concentration of SDS seems to be the best concentration for working in the environment of such species.
- d) For pre micellar (1.0mM) concentration lower than CMC (10mM) of SDS, this was found to be the most effective concentration for all the analytes. The reductions of the signal intensities were observed more or less proportional to acid concentrations. The HNO₃ has been observed to follow the same consistent behavior as for pre-micellar and micellar phases.

As the objective of this work is to evaluate the combined effect of HNO₃ and SDS on ICP-AES, thus individual effect of HNO₃ and SDS on each analyte has been investigated thoroughly as shown in Fig. 1 and Fig. 2 respectively, while Fig. 3 evaluates the changes in analytical signals under the influence of HNO₃ plus SDS.

Fig. 1 shows the different signal intensities in a range 0.01% to 2.0% of HNO₃. Slight suppression in signal intensity was observed, mainly when the acid concentration reaches to 0.5% - 2.0%. This factor also varies with the addition of surfactant concentration. Intensities of the analytes under study are not identical in acid concentration and attain different patterns. This manifests itself in the scatter

of analytical signals for different elements as reported in Table-1. Enhancement of the signals has been observed from 0.01% to 1.0% for all the analytes relatively except Cd, Pb and Ni. Relative intensity of Cd reasonably normalized with standard while shows slight enhancement at 1.0% and 1.5% HNO₃. In case of Pb the depression of the signals were observed at 0.01% to 0.2% then signal reaches near to blank. In case of Ni at 0.1% and 0.2% HNO₃ shows enhancement and then as acid concentration increases reduction of the signals were observed. Effect of HNO₃ on all other analytes seems to be identical, as the maximum enhancement occurred at 0.1% and then signal decreases with the increase in acidity. Pb, Cu and Ni intensities show prominent reduction at 0.5% to 2.0% HNO₃ where as all other analytes are near blank in this acid range.

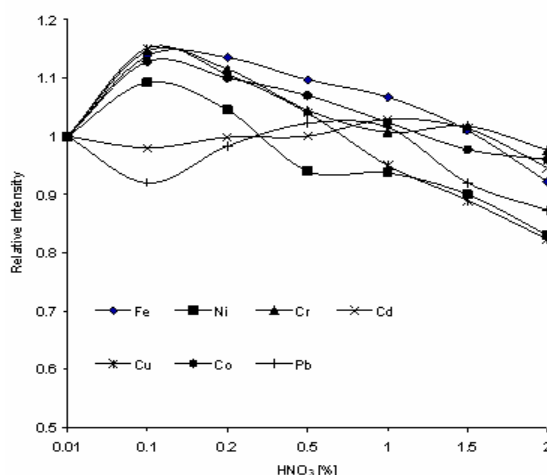


Fig. 1: Influence of nitric acid concentration on different analytes in ICP-AES.

Table-1: Coefficient of variance for analytes under the influence of HNO₃ and SDS at different concentrations studied in ICP-AES.

SDS+HNO ₃	Ni	Cr	Co	Pb	Cd	Fe	Cu
1.0mM SDS+ 0.01% HNO ₃	1.92	1.55	0.58	1.83	3.36	0.00	3.24
10mM SDS+ 0.01 % HNO ₃	2.73	0.00	1.83	3.46	2.53	2.92	2.57
50mM SDS+0.01% HNO ₃	1.78	2.87	2.57	1.02	0.48	1.49	3.55
1.0mM SDS+0.2 % HNO ₃	1.71	1.02	2.63	4.01	1.41	1.73	4.97
10mM SDS + 0.2 % HNO ₃	2.71	2.04	3.16	2.68	0.73	2.08	1.37
50mM SDS + 0.2 % HNO ₃	2.42	2.50	2.26	0.84	1.50	1.63	3.50
1.0mM SDS +0.5 % HNO ₃	3.90	3.50	3.44	4.29	2.92	0.00	1.83
10mM SDS + 0.5 % HNO ₃	2.16	1.93	2.13	4.39	2.83	1.39	4.29
50mM SDS + 0.5 % HNO ₃	4.30	4.32	1.64	3.25	1.55	2.92	4.67
1.0mM SDS+ 1.0 % HNO ₃	2.72	3.61	3.02	2.14	3.45	0.00	2.33
10mM SDS + 1.0 % HNO ₃	1.75	3.89	3.22	1.49	3.11	2.11	3.53
50mM SDS + 1.0 % HNO ₃	3.14	3.94	0.80	0.00	2.31	2.86	3.73
1.0mM SDS +1.5 % HNO ₃	4.82	3.31	2.72	3.15	2.55	1.76	0.82
10mM SDS + 1.5 % HNO ₃	3.04	3.16	3.33	2.63	2.17	2.92	4.15
50mM SDS + 1.5 % HNO ₃	3.59	3.37	1.74	1.90	3.01	0.00	3.50
1.0mM SDS + 2.0 % HNO ₃	2.95	0.00	0.00	4.16	1.59	0.00	3.54
10mM SDS + 2.0 % HNO ₃	3.42	0.00	0.83	2.86	2.67	3.68	2.75
50mM SDS + 2.0 % HNO ₃	1.54	0.00	2.33	0.00	3.89	1.70	4.06

Fig. 2 shows a unique behavior of analytes under the influence of SDS. The effect of pure SDS from pre-micellar to post micellar concentration has been investigated. The signal intensities of each analyte followed relatively the same pattern of enhancement and suppression with SDS concentration. In this case maximum enhancement for Cd in pre-micellar and maximum depression for Co and Pb in post micellar has been observed. At pre-micellar phase all the analytes show enhancement of signals while at critical micelle concentration falls near to blank, whereas at post micellar SDS concentration show depression in signals. It has been observed that the physical parameters such as surface tension, viscosity and density depending upon SDS concentration may affect uptake and nebulisation process, hence reduction or enhancement of the signals. Fig. 3 describes the effect of SDS under the influence of HNO₃. The anionic nature of SDS plus the oxidizing nature of the HNO₃ alters the signal intensities of each analyte relatively when compared with Fig. 1 and Fig. 2. Maximum enhancement of the signals for all the analytes at CMC (10mM; critical micelle concentration) has been observed at all the acidic values with different intensities. The depressions at CMC are also above the blank values. The trend of the acid effect i.e. depression of signals with increase in acidity also observed in the presence of SDS with different intensities.

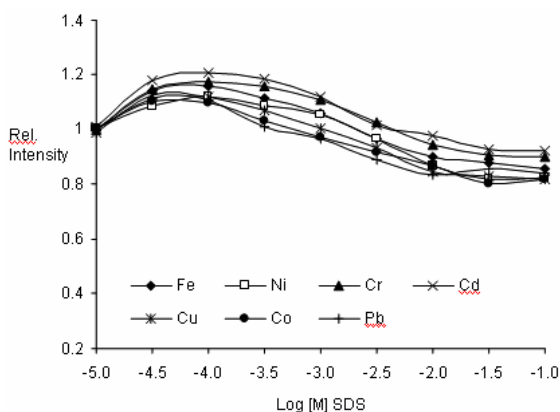


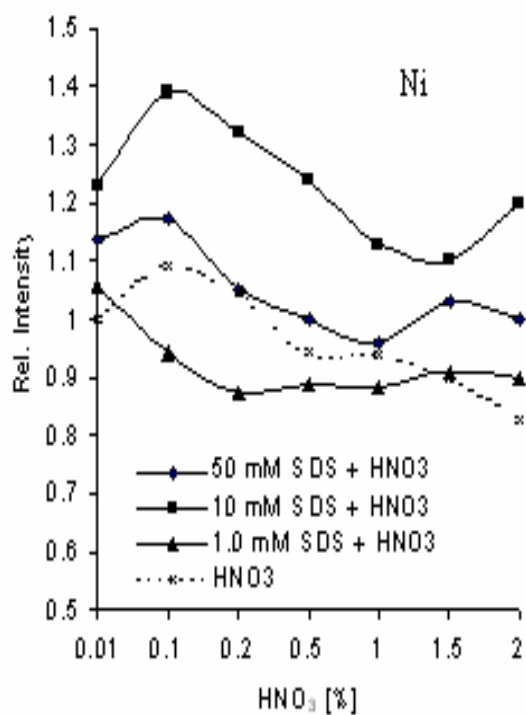
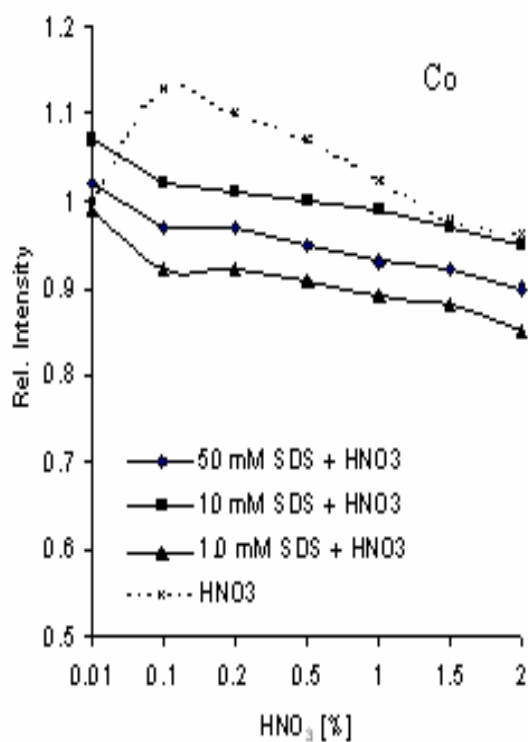
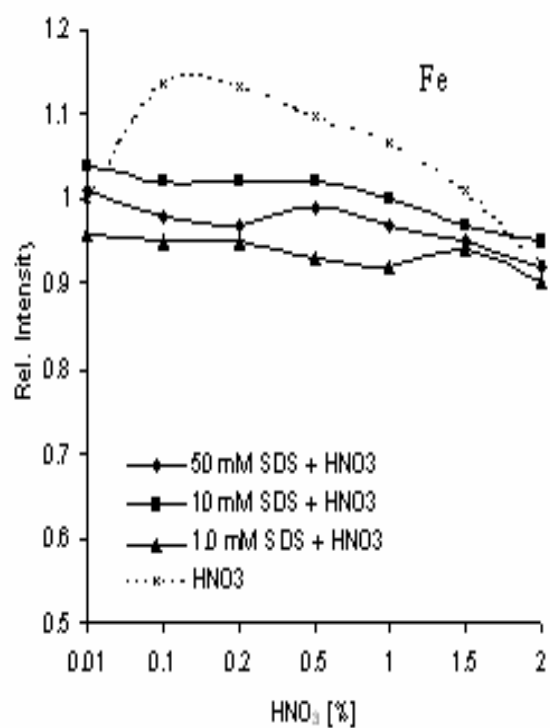
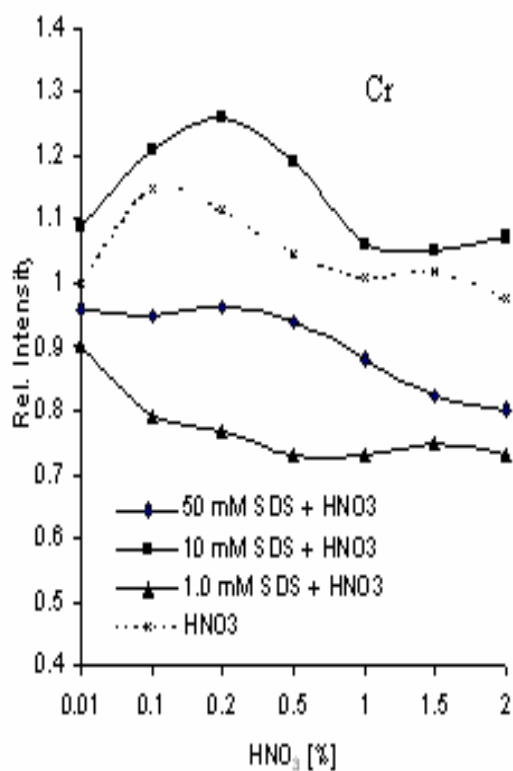
Fig. 2: Effect of SDS on the determination of analytes in ICP-AES.

In case of Cr & Ni described in Fig. 3, both the analytes behaving in the similar fashion with the difference in intensity levels. Signal enhances from 0.01% and then decrease with the concentration of HNO₃ till 2.0%. For Cr the micellar concentration enhances the signals more than pure acid signals (as shown by dotted line), where as for Ni the post micellar concentration shows the signals near the

acidic line and somehow near the blank also. The maximum enhancement has been observed with Cu about 45% at 0.01% HNO₃. It is observed that by ignoring 0.01% HNO₃, (from micellar and post micellar concentrations) the trend of HNO₃ effect as reduction of signal with increase in acid seems very minute, whereas a continuous decrease in signals pre-micellar phase with the increase in acidity is investigated. Thus variation in intensities shows the effect of SDS, which becomes linear even but the difference of the signal intensity for 1mM; pre-micellar, 10mM; micellar and 50mM for post micellar concentrations.

In Fig. 3 Fe and Co having similar approach of signal enhancement or reduction is observed, though the acid effect also shows the same behavior for these analytes. For Fe the intensity difference is very small in between the three phases of SDS. The micellar phase just falling near to the blank i.e. with the relative intensity near 1.0; however other two phases are also very close to it. The intensity enhances from 0.01% to 0.2% and then slightly falls till 2.0% HNO₃. However in pre micellar concentration there is depression in signal intensity from 0.01% till 0.5% then slightly enhances. As far as Co is concerned there is equal intensity difference between all the three concentrations of SDS at each acid concentration. By observing signal intensity as micellar > post micellar phase, micellar phase falls near the blank and shows maximum enhancement at 0.01% HNO₃.

In case of Cd an irregular pattern is observed. Signal intensity for micellar phase enhances as compared to other two phases. Pre micellar phase seems to be relatively closed to the acid line and to the blank as well, except at 0.01% and 1.0% HNO₃. The maximum enhancement of the signal is investigated at 0.01% concentrations of acid, which is greater than Fe and Co. It has been investigated that the collective effect of SDS and HNO₃ on Pb is rather different from all other analytes. In Fig. 1 and Fig. 2, Pb shows the compromised behavior with other analytes when treated individually with SDS and HNO₃. The maximum depression of the intensity has been observed in the pre-micellar phase, which relates with the acid concentration from 0.01% to 0.5% and then little enhances with the increase of SDS and acid concentrations. Maximum enhancement has been observed for Cu in micellar as well as in post-micellar phase, while the maximum reduction occurred for Pb in the range of 0.2%-0.5% of HNO₃.



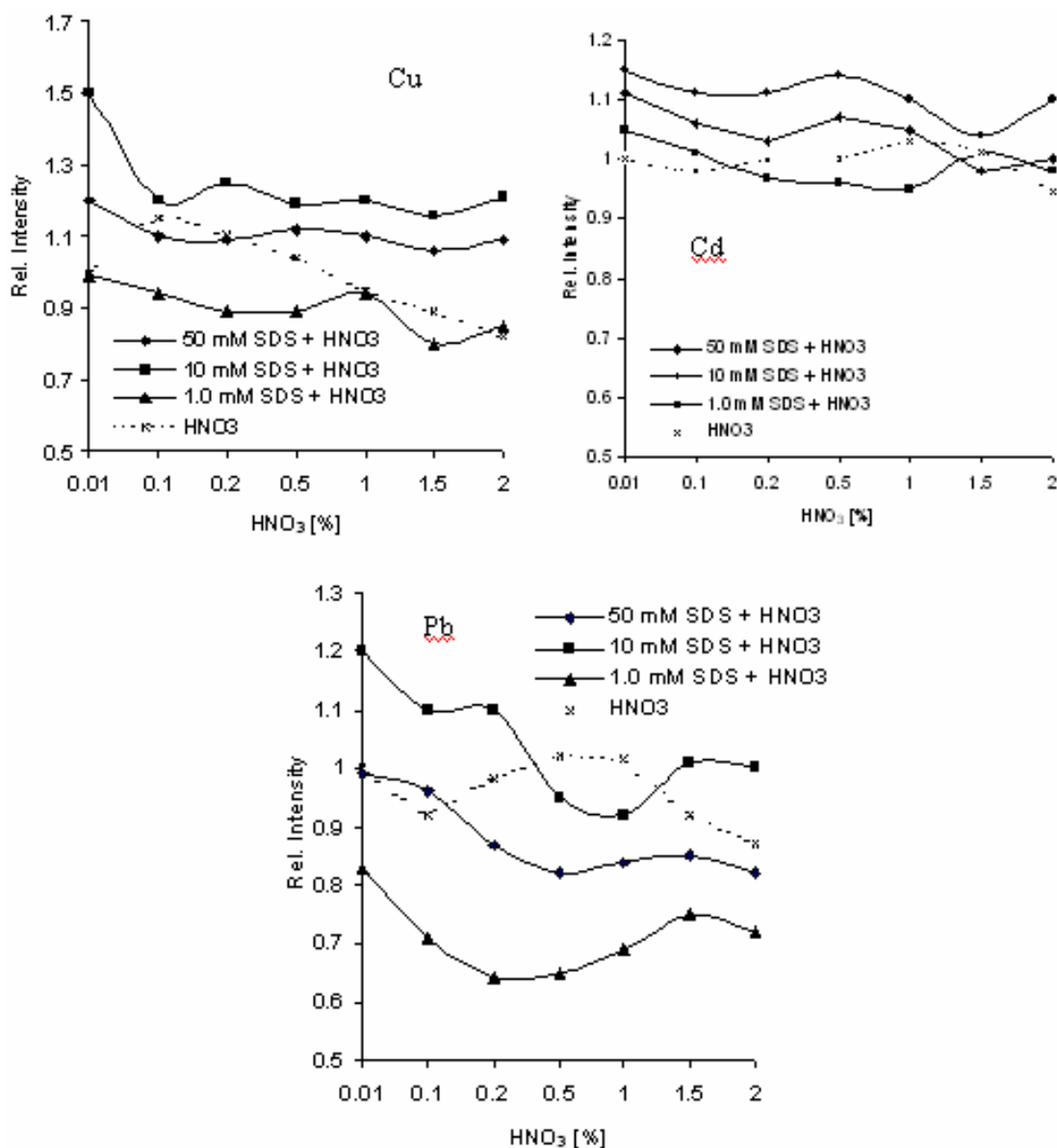


Fig. 3: Effect of SDS and HNO₃ on different analytes in ICP-AES.

Surfactants in dilute solutions below CMC act as strong electrolytes, and this property may lead to lowering the surface tension [18], thus expected to change the behavior of the analytes being nebulised. At CMC or further above the CMC this effect is expected to be gradually modified which restoring the original behavior of the system as a whole. From Figs. 1-3, it has been observed that the signal enhancement and suppression directly depends on the surfactant concentration used, while the effect of the HNO₃ has also been observed along with and without surfactant. Signal enhancement was also due the

concentration of the SDS, which physically describe the lowering of surface tension and viscosity of the solutions as well. The analytes may act as the counter ions of the micelles and may affect mainly due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups, consequently decreased electrical repulsion between analytes and micelles.

The magnitude of the depression or enhancement apparently collectively depends on the acid as well as SDS, but also on the energy of acid

molecules. The HNO_3 affects the pH value of the system but it may also act as the electrolytes for the present situation of the micellar system [19] thus, acid effects in inductively coupled plasma can be related with the action of different factors. Acids affect the process of nebulisation introduction into plasma; they change, in a complex manner, the physical conditions in plasma and finally, the analytical signals can depend on the chemical nature of acid and analyte.

The total effect of the electrolytes appears to approximate the sum of its effect on various parts of the solute molecule in contact with the aqueous phase [20]. Since the hydrophilic groups are in contact with the aqueous phase in both monomeric as well as in micellar form, while the hydrophobic only in the monomeric form. So the system involves the adjustment of the counter ion and electrolytes along with the surfactant in both monomeric and micellar forms. Normally in the case of nitric acid, the effect as counter ions is observed very little, which show decreasing effect of the micellisation [21]. The anionic surfactants (SDS) having the opposite charge to metal ions appeared to be more effective as compared to the cationic and nonionic surfactants as well as with alcohols which also enable to reduce the surface tension [22, 23].

Statistical analysis is also made for the validation of method by calculating coefficient of variance via relative standard deviation for the accuracy and precision of the present work. Table-2 describes as a whole coefficient of variance for all the analytes at all working concentrations of SDS with HNO_3 . The Coefficient of variance was calculated with three consecutive reading for each set of experiment. Hence the method is found to be a convenient, rapid and reproducible for the determination of elements in the presence of anionic surfactant and HNO_3 by the ICP-AES.

Decrease in surface tension and viscosity change in aqueous solutions, play an important role for smaller droplets and should enhance the intensity solutions [24-26] of the analytes. The nebuliser with higher flow rates (velocity), resulting in smaller droplets size by hydrodynamic compaction and by increasing the rate of evaporation during formation and transport, results in the enhancement of the intensities [25]. Therefore micellar concentration is in reasonably good working range as compared to pre-micellar and post-micellar concentrations. Solvent transport efficiency is the fraction of the solvent pumped to the nebuliser that reaches the plasma so have been calculated for pneumatic Meinhard type

nebuliser for some sample solutions including surfactants and acids by using indirect method [27]. Experimental measurements of transport efficiencies found in the range of 0.7%-2.2% show a good agreement with the results from the literature [28].

The Aerosol Ionic Redistribution (AIR) theory of Borowiec *et.al* [29] proposed mechanism of analyte transport to the flame by the interaction of spectator ions of the anionic sulphate head group of the sodium dodecyl sulphate with the metal cation of the analyte, enrichment occurs at the double layer on the outside surface of the large drops. Fig. 4 communicates about the stripping action; as the bigger drops passes through stripping action and results into smaller droplets (secondary and tertiary) are nebulised and carried into the flame, in result increases the analytes intensity. The physical properties may effects the uptake rate of the solution by increasing the viscosity as well as the density of the solution while simultaneously decreases the intensity of the analytes. It is also considered that aerosol ionic redistribution is extremely dependent upon droplet size, due to the reduction in surface tension in the presence of SDS, which in turn highly affects sensitivity to intensity. As the surfactant have been used along with acid in this study to develop the understanding for the modification of the analytical system, resulting in improved nebulisation efficiency for all the analytes in the micellar system and showing good agreement with previous workers [30, 31].

Experimental

Equipment

A Jobin Yvon ICP system from France, consisting of JY 2300 plasma source JY-32 polychromator and JY 38 monochromator was used. The detail of the equipment and operating conditions as used for the evaluation of surfactants effect are given in Table-2. The nebuliser used in this study was a concentric all glass Meinhard type, and was employed with a conventional Scott type chamber.

Chemicals

Sodium Dodecyl Sulphate; SDS ($\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$) an anionic surfactant was chosen on the basis of commercial availability and having broad range of biological and chemical applications and purchased from Fluka. Nitric acid was of Purus grade from Merck. Doubly distilled deionised water (DDW) was used for all sample preparation during this work.

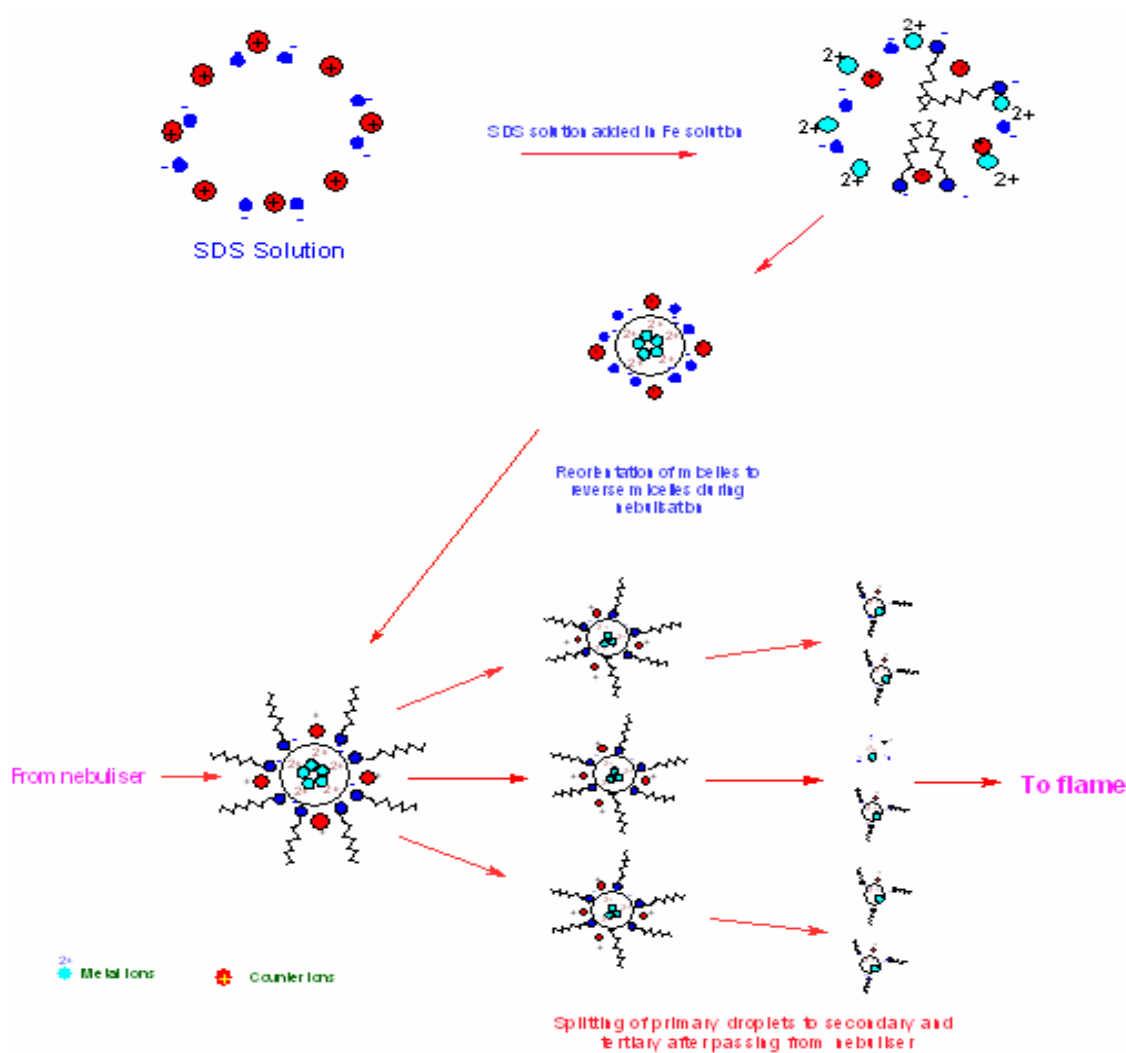


Fig. 4: Proposed model for the nebulised surfactant—metal ions solution and stripping of metal to plasma flame.

Table-2: Equipment and Operating Conditions.

i) Spectrometer System	A computer controlled monochromator JY-38 (VHR) with 3600 grooves/mm holographic (Jobin Yvon, France)
ii) R.F Source	JY 2300, Crystal regulated 40.68 MHz generator
iii) Plasma Torch	De-mountable modular
iv) Nebuliser	Meinhard type.
v) Computer	Apple-IIe
vi) Detector	P.M. tube R 106 HA
Operating Conditions	
vii) R.F. Power	1.0 K.W
viii) Reflecting Power	< 5W
ix) Viewing height	10-20 mm above the load coil
x) Slits	Entrance 25 um, Exit 30um
xi) Integration Time	1000ms
xii) Argon Gas flow rates	60psi
a) Plasma	12.0L/min
b) Carrier Gas	0.8 L/min
c) Coating Gas	0.35 L/min

Reagents and Solutions

All sample solutions used were prepared by V/V. Single element standards from Spex, were used for 5ppm solutions of Cr, Fe, Co, Ni, Cu, Cd and Pb. Stock solution of SDS was prepared by dissolving 2.88g in 100mL of SDS in DDW. Further 5ppm analytes were added in SDS matrix for a set of three concentrations i.e. (a) Concentration above CMC, (b) At CMC and (c) Below CMC of the surfactant. Nitric acid concentration used in range of 0.01% to 2% for each analyte sample solution.

Procedure

All sample solutions (for each 5ppm analyte) were prepared in 25ml volumetric flasks. Sample solutions were prepared and analysed in triplicate after confirming the CMC (for micellar and post micellar conc. by conductivity method) by availing two hours rest time. Coating gas has been used to protect the formation and as well as for the better transportation of aerosols to the plasma.

All solutions were nebulised and emission intensities were measured at prominent analyte spectral lines as shown in Table-2 by following the instrumental compromised conditions. Three different sets of sample solutions were prepared and samples were nebulised by attaining the following sequence.

- i) Seven different analytes sample solutions of 5 ppm in concentration range of HNO₃ (0.01% to 2.0%).
- ii) Set of three SDS samples solutions for pre-micellar, micellar and post micellar concentrations with each seven analytes i.e. Cr, Fe, Co, Ni, Cu, Cd and Pb.
- iii) Sample solutions containing solutions i) plus ii).

The relative intensity of all the sample solutions with and without SDS and acid for each analyte has been measured by normalizing with standards of analytes in doubly distilled deionised water.

Relative intensity was calculated as.

$$I_R = \frac{I_s - I_{sb}}{I_a - I_b}$$

where

- I_R =Relative Intensity.
 I_a =Intensity of Analyte.
 I_b =Intensity of Analyte blank.
 I_s =Intensity of Surfactant plus analyte.
 I_{sb} =Intensity of blank surfactant.

Conclusion

It is clear from the data that all effects of the surfactant and the acid depend on the specific metal ions. The enhancement and depression may be explained by some physical change in the aerosol characteristics (droplet size distribution, nebuliser and transport efficiency) but strongly by a variation of the chemical properties of the aerosol. Thus a strong effect of the surfactant and acid is observed by the change in the anions and cations concentrations. The nebulization process being critical for such studies, due to its vulnerability to the changes in the surface tension and somehow viscosity of the analytes samples at pre-micellar, micellar and post micellar surfactant concentration, may suggest a logical explanation for some of the experimental results. Again the oxidizing nature of the matrix may lead to an uncertainty factor and a more complex behavior suggesting further extensive studies. Beside it a more rigorous approach required to correlate the aerosol particle size measurements and correlation of this data to the noticed over all depression or the enhancement effects. It should be noted that the study of the influence of the counter ions need to develop more precisely for further work, as it seems that the influence of the anions is as important as cations. Keeping in view the results presented, at this stage, one may of the opinion that small concentrations of the surfactants do affect the final analyte signals and thus introduce a factor of uncertainty in such analytical manipulations.

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