



e-ISSN: 2319-8753 | p-ISSN: 2347-6710

IJRSET

International Journal of Innovative Research in
SCIENCE | ENGINEERING | TECHNOLOGY

INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 11, Issue 7, July 2022

ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA

Impact Factor: 8.118

 9940 572 462

 6381 907 438

 ijirset@gmail.com

 www.ijirset.com

Effect of Temperature on the Autoxidation of Sulfur Dioxide in the Presence of Alcohols under Condition Related to Tropospheric

Dr. Manoj Kumar

Assistant Professor, Chemistry, Govt. College, Kota, Rajasthan, India

ABSTRACT: The heterogeneous oxidation of sulfur dioxide by ozone on CaCO_3 was studied as a function of temperature (230 to 298 K) at ambient pressure. Oxidation reactions were followed in real time using diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) to obtain kinetic and mechanistic data. From the analysis of the spectral features, the formation of sulfate was identified on the surface in the presence of O_3 and SO_2 at different temperatures from 230 to 298 K. The results showed that the heterogeneous oxidation and the rate of sulfate formation were sensitive to temperature. An interesting stage-transition region was observed at temperatures ranging from 230 to 257 K, but it became ambiguous gradually above 257 K. The reactive uptake coefficients at different temperatures from 230 to 298 K were acquired for the first time, which can be used directly in atmospheric chemistry modeling studies to predict the formation of secondary sulfate aerosol in the troposphere. Furthermore, the rate of sulfate formation had a turning point at about 250 K. The sulfate concentration at 250 K was about twice as large as that at 298 K. The rate of sulfate formation increased with decreasing temperature at temperatures above 250 K, while there is a contrary temperature effect at temperatures below 250 K. The activation energy for heterogeneous oxidation at temperatures from 245 K to 230 K was determined to be $14.63 \pm 0.20 \text{ kJ mol}^{-1}$. A mechanism for the temperature dependence was proposed and the atmospheric implications were discussed.

KEYWORDS: sulfur dioxide, tropospheric, temperature, autoxidation, alcohols, heterogenous, aerosol, pressure

I. INTRODUCTION

Tropospheric propagation describes electromagnetic propagation in relation to the troposphere. The service area from a VHF or UHF radio transmitter extends to just beyond the optical horizon, at which point signals start to rapidly reduce in strength. Viewers living in such a "deep fringe" reception area will notice that during certain conditions, weak signals normally masked by noise increase in signal strength to allow quality reception. Such conditions are related to the current state of the troposphere.[1,2]

Tropospheric propagated signals travel in the part of the atmosphere adjacent to the surface and extending to some 25,000 feet (8 km). Such signals are thus directly affected by weather conditions extending over some hundreds of miles. During very settled, warm anticyclonic weather (i.e., high pressure), usually weak signals from distant transmitters improve in strength. Another symptom during such conditions may be interference to the local transmitter resulting in co-channel interference, usually horizontal lines or an extra floating picture with analog broadcasts and break-up with digital broadcasts. A settled high-pressure system gives the characteristic conditions for enhanced tropospheric propagation, in particular favouring signals which travel along the prevailing isobar pattern (rather than across it). Such weather conditions can occur at any time, but generally the summer and autumn months are the best periods. In certain favourable locations, enhanced tropospheric propagation may enable reception of ultra high frequency (UHF) TV signals up to 1,000 miles (1,600 km) or more.[3,4]

The observable characteristics of such high-pressure systems are usually clear, cloudless days with little or no wind. At sunset the upper air cools, as does the surface temperature, but at different rates. This produces a boundary or temperature gradient, which allows an inversion level to form – a similar effect occurs at sunrise. The inversion is capable of allowing very high frequency (VHF) and UHF signal propagation well beyond the normal radio horizon distance.

The inversion effectively reduces sky wave radiation from a transmitter – normally VHF and UHF signals travel on into space when they reach the horizon, the refractive index of the ionosphere preventing signal return. With temperature inversion, however, the signal is to a large extent refracted over the horizon rather than continuing along a direct path into outer space.



Fog also produces good tropospheric results, again due to inversion effects. Fog occurs during high-pressure weather, and if such conditions result in a large belt of fog with clear sky above, there will be heating of the upper fog level and thus an inversion. This situation often arises towards night fall, continues overnight and clears with the sunrise over a period of around 4 – 5 hours.

Tropospheric ducting is a type of radio propagation that tends to happen during periods of stable, anticyclonic weather. In this propagation method, when the signal encounters a rise in temperature in the atmosphere instead of the normal decrease (known as a temperature inversion), the higher refractive index of the atmosphere there will cause the signal to be bent. Tropospheric ducting affects all frequencies, and signals enhanced this way tend to travel up to 800 miles (1,300 km) (though some people have received "tropo" beyond 1,000 miles / 1,600 km), while with tropospheric-bending, stable signals with good signal strength from 500+ miles (800+ km) away are not uncommon when the refractive index of the atmosphere is fairly high.

Tropospheric ducting of radio and television signals is relatively common during the summer and autumn months, and is the result of change in the refractive index of the atmosphere at the boundary between air masses of different temperatures and humidities. Using an analogy, it can be said that the denser air at ground level slows the wave front a little more than does the rare upper air, imparting a downward curve to the wave travel.[5,6]

Ducting can occur on a very large scale when a large mass of cold air is overrun by warm air. This is termed a temperature inversion, and the boundary between the two air masses may extend for 1,000 miles (1,600 km) or more along a stationary weather front.

Temperature inversions occur most frequently along coastal areas bordering large bodies of water. This is the result of natural onshore movement of cool, humid air shortly after sunset when the ground air cools more quickly than the upper air layers. The same action may take place in the morning when the rising sun warms the upper layers.[7,8,9]

Even though tropospheric ducting has been occasionally observed down to 40 MHz, the signal levels are usually very weak. Higher frequencies above 90 MHz are generally more favourably propagated.

High mountainous areas and undulating terrain between the transmitter and receiver can form an effective barrier to tropospheric signals. Ideally, a relatively flat land path between the transmitter and receiver is ideal for tropospheric ducting. Sea paths also tend to produce superior results.[10,11]

In certain parts of the world, notably the Mediterranean Sea and the Persian Gulf, tropospheric ducting conditions can become established for many months of the year to the extent that viewers regularly receive quality reception of signals over distances of 1,000 miles (1,600 km). Such conditions are normally optimum during very hot settled summer weather.

Tropospheric ducting over water, particularly between California and Hawaii, Brazil and Africa, Australia and New Zealand, Australia and Indonesia, Strait of Florida, and Bahrain and Pakistan, has produced VHF/UHF reception ranging from 1000 to 3,000 miles (1,600 – 4,800 km). A US listening post was built in Ethiopia to exploit a common ducting of signals from southern Russia.[12,13]

Tropospheric signals exhibit a slow cycle of fading and will occasionally produce signals sufficiently strong for noise-free stereo, reception of Radio Data System (RDS) data, and solid locks of HD Radio streams on FM, noise-free, color TV pictures, or stable DTV reception, as well stable DAB Radio reception. With DVB-T it can also enable a wide SFN, so long as the two transmitters are within a guard interval and are almost equidistant from the receiver as well as synchronised. However, if they aren't synchronised and aren't equidistant they will interfere with each other.

Virtually all long-distance reception of digital television occurs by tropospheric ducting (due to most, but not all, TV stations broadcasting in the UHF band).

II. DISCUSSION

Alcohols commonly present both in urban and in rural atmosphere add to the group of pollutants termed volatile organic compounds (VOCs). The gas-phase concentration of ethanol may be even as high as 226ppbv, whereas the maximum concentration determined, for instance, for phenol is only 2.5ppbv (Isidorov, 2001). Since alcohols are rather well water soluble, their reactivity with respect to other chemical species contained in the atmospheric aqueous phase (cloud waters, wet aerosols/fogs) becomes of interest, particularly with the view to the radical intermediates in the autoxidation of aqueous sulphur dioxide. The aqueous-phase concentration of methanol and ethanol assumed as representative for urban atmosphere conditions is 1.8×10^{-6} and $3.1 \times 10^{-7} M$, respectively (Herrmann et al., 2000). The interaction between alcohols and the SO_2 oxidation intermediates may have a bearing on acidity formation in the atmosphere.

Bigelow (1898) was the first who found experimentally that alcohols, such as methanol, ethanol, propanol and butanol, slow down the reaction between sodium sulphite and air oxygen. His aim was to gain some quantitative data to widen the knowledge on catalysis in the sense of Berzelius. The inhibiting effect of aliphatic alcohols (ethanol, isopropanol, secondary butanol and benzyl alcohol) on the oxidation of sodium sulphite was then investigated by Alyea and Bäckström (1929) in a chain reaction theory-based study. These authors gave the following rate expression: $v_d = k_1 / (k_C + k_2)$, where the terms in the denominator represent two different ways by which the reaction chain breaking occurs, the first one corresponding to the action of the alcohol and the second one reflecting some other cause of chain breaking. The experiments described by the above equation were performed under alkaline conditions (initial pH 8.4). [14,15] Later, Bäckström (1934) developed the radical mechanism of the reaction between sodium sulphite and oxygen to show the probable contribution of such radicals as $\cdot\text{SO}_3^-$, $\text{SO}_4^{\cdot-}$ and $\text{SO}_5^{\cdot-}$ in the formation of a chain and to explain the previously observed alcohol inhibition by the reaction: $\text{RCH}_2\text{OH} + \text{SO}_5^{\cdot-} = \text{RCHO} + \text{SO}_4^{\cdot-} + \text{H}_2\text{O}$. The interests of further researchers were focused on gaining the direct experimental evidence for the reactivity of sulphonyl radicals with respect to alcohols, which resulted in proving the unshakable ability of these compounds to react with $\text{SO}_4^{\cdot-}$ (Ashmore, 1963; Gilbert et al., 1988; Dogliotti and Hayon, 1967; Clifton and Huie, 1989), whereas reactions with $\cdot\text{SO}_3^-$ and $\text{SO}_5^{\cdot-}$ occurred unimportant (Hayon et al., 1972). [16,17] A strong impulse to develop experimental studies on the kinetics and products of sulphate radical-alcohol reactions was when it occurred clear that these reactions may be of importance in chemistry of atmospheric aqueous phase (Clifton and Huie, 1989; Wine et al., 1989; Warneck et al., 1994; Ziajka 1996, Ziajka 2001; Ziajka and Pasiuk-Bronikowska 1999, Ziajka and Pasiuk-Bronikowska 2000, Ziajka and Pasiuk-Bronikowska 2003). At this stage one of the main goals was to derive information about the reactivity of $\text{SO}_4^{\cdot-}$ toward different types of C-H bonds and determine rate constants for the reactions of this radical with a series of alcohols. The reactions were shown to proceed by a simple hydrogen abstraction mechanism. Another goal was to differentiate between radicals in the oxidation of S(IV) and thus to remove some uncertainties in understanding the overall reaction mechanism. The methanol inhibition of the uncatalysed autoxidation of HSO_3^- was investigated by Connick et al. (1995) to shed more light on a mechanism of initiation in the absence of transition metal ions. Connick and Zhang (1996) showed that in the presence of manganous ions the inhibition by methanol is more complex than indicated by simply adding to the overall reaction mechanism the step by which sulphate radicals are scavenged.

In this work the alcohols of well known reactivity with respect to sulphate radicals, like ethanol and 2-propanol, were chosen to allow us to settle the consistency between the S(IV) overall oxidation kinetics in the presence of these alcohols and the reaction mechanism including inhibition by the sulphate radical scavenging. We also believed that the better elucidated inhibition mechanism could occur helpful to determine the weakly known or yet unknown reactivity of such alcohols, like cis-verbenol, myrtenol and nopol.

III. RESULTS

Although the SO_2 oxidation by O_2 has been the subject of many studies, the mechanism of the reaction is far from settled. Both non radical and radical mechanism have been proposed. The atmospheric oxidation of SO_2 by O_2 in aqueous media has been the subject of numerous studies, and the subject matter of several reviews, monographs and papers, notably by Kuo et al. [1-11]. It is interesting to point out that reaction is strongly inhibited by alcohol, benzene, and other compounds. Pointing to the participation of radical intermediates [12-17]. Bigelow [18] was the first to observe the inhibiting effect of alcohols such as methanol, ethanol, propanol, butanol on the rate of the reaction between sodium sulfite and oxygen. The inhibiting effect of alcohols was investigated subsequently by Alyea et al. [19]. The other Organics studied are phenols [20] organic acids [21-23], benzene [24], toluene, naphthalene, paraffin oil [25], alpha-pinene, cis-verbenol [26], sobrerol [27], myrtenol [28]. The effect of aromatic amines i.e. aniline in atmospheric water on the transition metal-catalysed oxidation of S(IV) is not fully known yet and more work in this area is needed to understand these processes better. The purpose of the present study was to study the kinetics of the Ag(I) catalysed S(IV) oxidation and to determine the inhibiting effect of aniline on this process under different experimental conditions. [18,19]

IV. EXPERIMENTAL

The experimental procedure was exactly the same as described earlier [29]. All the chemicals used were AR grade and their solutions were prepared in doubly distilled water. The reaction were conducted in 0.15L Erlenmeyer flask, open to air and follow to passage of atmosphere oxygen. The flask was placed in a beaker which had an inlet at a lower part and an outlet at a outer part for circulating thermostatic water for maintaining the desired temperature $30 \pm 10^\circ\text{C}$. The reaction was initiated by adding the desired volume of Na_2SO_3 solution to the reaction mixture containing other additive such as buffer and catalyst. [20,21] The reaction mixture was stirred continuously and magnetically at 1600 ± 10 rpm to allow the passage of atmospheric oxygen and to save the reaction from becoming oxygen mass transfer controlled. The

kinetics was studied in acetate buffered medium in which the pH remained fixed throughout the entire course of reaction. For this purpose 10cm³ buffer made from sodium acetate (0.07mol L⁻¹) and acetic acid (0.03mol L⁻¹) for acidic medium were used (total volume 100cm³) for obtaining the desired pH. The kinetics were followed by withdrawing the aliquot samples periodically and titrating the unreacted S(IV) iodometrically. The reproducibility of replicate measurements was generally better than 10+1 %. All calculations were performed in MS Excel.[22,23]

Product Analysis

The qualitative test shows sulphate to be only oxidation product. For quantitative analysis, the reaction mixture containing catalyst and S(IV) in appropriate buffered solutions were constantly stirred for a sufficiently long time so as to ensure complete oxidation of S(IV). When the reaction was complete then S(VI) estimated gravimetrically by precipitating sulphate ions as BaSO₄ using standard procedure.

The product analysis showed the recovery of sulphate to be 98+1%, in all cases in agreement with eq. (1)

Preliminary investigation

The kinetics of both uncatalysed and Ag(I) catalysed and aniline inhibited reaction were studied in acidic medium in pH 4.95 and temperature 30°C. In both the cases the first order dependence of S(IV) was observed in the kinetics data treatment for the determination of first order rate constant k_1 was carried out from $\log [S(IV)]$ versus time, t . The plots were shown in Figure 1 It is obs. from Figure 1 that both the uncatalysed and Ag(I) catalysed autoxidation of S(IV) reaction are inhibited by aniline.

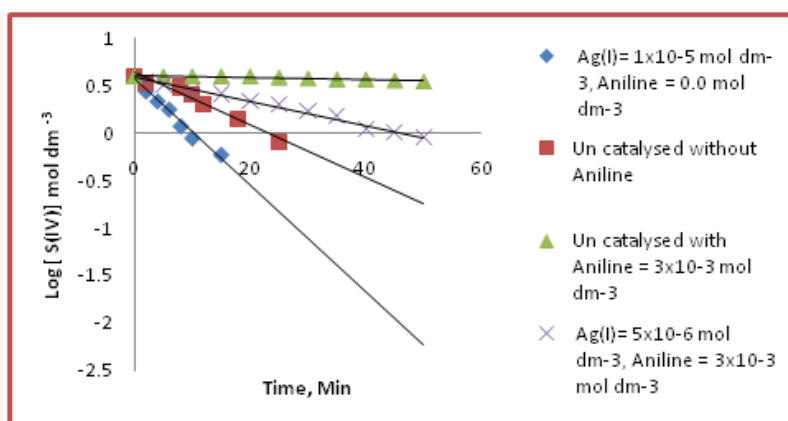


Figure 1: The disappearance of [S(IV)] with time in air saturated suspensions at [S(IV)] = 2×10^{-3} mol dm⁻³ at pH = 4.95, $t = 30^\circ\text{C}$.

◇ Ag (I) = 1×10^{-5} mol dm⁻³, [Aniline] = 0.0 mol dm⁻³.

□ Uncatalysed without aniline.

△ Uncatalysed with [Aniline] = 3×10^{-3} mol dm⁻³.

x Ag (I) = 5×10^{-6} mol dm⁻³, [Aniline] = 3×10^{-3} mol dm⁻³. [24,25]

V. CONCLUSIONS

Gupta et al. [34] studied the role of some organic organics on the oxidation of dissolved sulfur dioxide by oxygen in rain water medium and found it follows radical mechanism so free radical scavengers such as VOCs decelerate the S(IV) oxidation and control the rain water acidity [35]. Bigelow et al. [18] studied the effect of alcohols on the reactions between sodium sulphite and O₂ and found that the alcohols inhibited the reaction rate. Alyea et al. [19] studied the inhibiting effect of aliphatic alcohols on sodium sulphite in alkaline medium. Gupta et al. [34] studied the kinetics of environmentally important oxidation of S(IV) in acetate buffered medium in presence of Iron (III) in pH range 5.27- 5.70 and reported that addition of ethanol leads to decrease in reaction rate. Grgic et al. [36] studied about scavenging of SO₄⁻ radical anions by mono and dicarboxylic acids in the Mn(II) catalysed oxidation in aqueous solutions and reported that low molecular weight carboxylic acids have low reactivity towards sulphate radical anion.

Backstrom [19] proposed a radical chain mechanism for alcohol inhibited oxidation reaction between sodium sulphite and O_2 . [26,27,28]Gupta et al studied the influence of hydroxyl VOCs on the oxidation of S(IV) by oxygen and found VOCs inhibited the S(IV) oxidation. Grgic et al. [30] studied the inhibition effect of acetate, oxalate, format on Fe-catalysed autoxidation of S(IV) at pH 2.8, 3.7,4.5 and found that oxalate has strong inhibiting effect on reaction rate due to the decrease amount of catalytic activity of Fe+3 due to formation of complexion with oxalate. Bostjan et al. [29] studied the effect of carboxylic acid on Mn(II) catalysed oxidation of S(IV) and found that monocarboxylic acid exhibit strong inhibition and out of which acetic acid shows strong inhibition. The rate of uncatalysed and Ag(I) catalysed reaction is decelerated by the addition of aniline in the present study. Gupta et al. [12] reported that radical mechanism operate in those reaction in which the inhibition parameters lies 10^3 - 10^4 In the present study the value of inhibition parameter for uncatalysed and Ag(I) catalysed autoxidation of S(IV) by aniline are found to be in the range 10^3 - 10^4 These values are in the same range as reported by Gupta et al. [15] This is strongly support the radical mechanism in the present case too based on the observed results. The free radical mechanism is very complex, the present work close to the experimental condition of Connick et al. [30].

REFERENCES

1. "DXing.com – The Web Resource for Radio Hobbyists". Universal Radio Research. November 2, 2016. Retrieved November 12, 2016.
2. ^ "Rijn Muntjewerff's TV DX Netherlands 1961–2005". Todd Emslie's TV DX Page. Todd Emslie. Retrieved November 12, 2016.
3. ^ "WTFDA FM ALL-TIME DISTANCE RECORDS – AS OF 2/1/16". WTFDA.org (Worldwide TV-FM DX Association). February 1, 2016. Retrieved November 12, 2016.
4. ^ "FERNANDO GARCIA: North America's champion of tropo TV DX". THE TV DX EXPOSITION. Retrieved November 12, 2016.
5. ^ "JEFF KRUSZKA'S RECORD-BREAKING DTV TROPO as received in south Louisiana". THE TV DX EXPOSITION. Retrieved November 12, 2016.
6. ^ Emel. "XPLORADIO: 9.12.2004 – gigantyczne tropo UHF i FM!". XPLORADIO. Retrieved 2018-07-01.
7. ^ <https://youtube.com/cPsi0GPeiXc>
8. ^ "TROPO MA to FL!!!! 97.9 WRMF". Worldwide TV-FM DX Association; WTFDA Forums. June 2007. Retrieved November 12, 2016.
9. ^ "My FM-DX Records". XPLORADIO. Maciej Ługowski. Retrieved 2018-07-01.
10. ^ EMEL DX (2011-09-19), FM DX: 1700 KM TROPO!, archived from the original on 2021-12-20, retrieved 2017-10-10
11. ^ "Kjell, SM7GVF (ex SM4GVF) – Best DX worked by SM7GVF from JO77GA". Retrieved November 12, 2016.
12. ^ "WA5IYX DTV DX Screen Captures". Retrieved November 12, 2016.
13. ^ "Aug 24–25 2009 Es (er, Tropo)". Worldwide TV-FM DX Association; WTFDA Forums. August 2009. Retrieved November 12, 2016.
14. ^ https://www.fmlist.org/fm_logmapt.php?datum=2016-09-28&band=Tropo&target=ALL&rxin=ALL
15. ^ "FM DX Tropo Log – Tomaszów Mazowiecki, Poland".
16. ^ Archived at Ghostarchive and the Wayback Machine: "[Tropo] 98.5 – DR P4 – Holstebro/Mejrup, Denmark (1960 km)". YouTube.
17. Huie RE, Neta P (1984) Chemical behaviour of SO₃- and SO₅- radicals in aqueous solutions. *Journal of Physical Chemistry* 88(23): 5665-5669.
18. Bigelow SL (1988) Catalytic effects in the oxidation of sodium sulfite by air oxygen. *Zeitschrift fuer Physikalische Chemie* 26: 493-532.
19. Alyea HN, Backstrom HLJ (1929) The inhibitive action of alcohols on the autoxidation of sodium sulfite. *Journal of American Chemical Society* 51(1): 90-107.
20. Altwicker ER (1980) Advances in Environmental Sciences and Engineering. In: Pfaffin JR & Ziegler EN (Eds.), Gordon and Breach Science Publishers, New York, USA, pp. 80-91.
21. Lee YJ, Rochelle GT (1987) Oxidative degradation of organic acid conjugated with sulfite oxidation in flue gas desulfurization: products, kinetics and mechanism. *Environ Sci Technol* 21(3): 266-271.
22. Grgic I, Dovzan A, Bercic G, Hudnik V (1998) The effect of atmospheric organic compounds on the Fecatalyzed S(IV) autoxidation in aqueous solution. *Journal of Atmospheric Chemistry* 29(3): 315-337.
23. Wolf A, Deutsch F, Hoffmann P, Ortner HM (2000) The influence of oxalate on Fe-catalyzed S(IV) oxidation by oxygen in aqueous solutions. *Journal of Atmospheric Chemistry* 37(2): 125-135.
24. Ziajka J, Beer F, Warneck P (1994) Iron-catalyzed oxidation of bisulfite aqueous solution: Evidence for a free radical chain mechanism. *Atmospheric Environment* 28(15): 2549-2552.



25. Pasuik BW, Bronikowski T, Ulejczyk M (1997) Solubilization of organics in water coupled with sulfite Autoxidation. *Water Research* 31(7): 1767-1775.
26. Pasuik BW, Bronikowski T, Ulejczyk M (1998) Chemical interactions of aqueous phase pollutants: Sulfur dioxide and sobrerol. In: Schurath U & Roselieb R (Eds.), Aachen, Germany, p. 1-4.
27. Pasuik BW, Bronikowski T, Ulejczyk M (1999) Oscillations in the rate of S(IV) autoxidation inhibited by sobrerol. In: Vogt R & Axelsdottir G (Eds.), Aachen, Germany, pp. 195-198.
28. Pasuik BW, Bronikowski T, Ulejczyk M (2000) Transformation of atmospheric constituents and pollutants induced by S(IV) Autoxidation-Chemistry and kinetics. *Chemical Mechanism Development*, pp. 123-126.
29. Sameena B, Faiyaz H, Prasad DSN (2013) Kinetics of formic acid inhibited uncatalysed and Co₂O₃ catalysed autoxidation of S(IV) in alkaline medium. *Pelagia research library* 4(1): 122-131.
30. Irena W, Anna M (2008) Mn(II) catalysed and its inhibition by acetic acid in aqueous solutions. *Journal of Atmospheric Chemistry* 60(1): 1-17.



INNO SPACE
SJIF Scientific Journal Impact Factor
Impact Factor: 8.118



ISSN INTERNATIONAL
STANDARD
SERIAL
NUMBER
INDIA



INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

 **9940 572 462**  **6381 907 438**  **ijirset@gmail.com**



www.ijirset.com

Scan to save the contact details