International Journal of Global Innovations and Modern Research
Abbreviated Key Title: IJGIMR
ISSN (Online): 3108-1789
Published By Books Arcade, Delhi, India.

Volume-1 | Issue-1 | January - June 2026 |

ORIGINAL ARTICLE

DETERMINATION OF SOME SULPHONYL CHLORIDES

Sanjay Kumar Jasrotia[1] and Ved Parkash Patial[2]

[1] Associate Professor in Chemistry, Government College Dharamshala, Himachal Pradesh, India
E-mail: sanjay_jasrotia@yahoo.co.in
[2] Professor of Chemistry & Dean Academics, Sri Sai University Palampur, Himachal Pradesh, India
E-mail: patialvp@yahoo.in

Corresponding Author:
Shalu Shukla
Assistant Professor in Pharmacy,
Chandigarh Group of Colleges,
Landran, Mohali, Punjab, India.

Funding: This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

ABSTRACT

Sulphonyl chlorides, RSO_2Cl are compounds of extensive economical, diagnostic and synthetic importance. Subsequently, their determination is of enormous opportunity and countless value. These find significant uses in leather manufacture-tanning, as fat liquoring mediators and for leather impregnation1. Sulphonyl chlorides support as appreciated substances in certification and determination of primary and secondary amines and phenols2. They serve as significant and inexpensive intermediates for the synthesis of economically significant compounds such as sulphonamides, sulphonic acids, sulphonyl hydrazides, sulphones, sulphinic acids and mercaptans. Sulphonamides find wide use in chemotherapy as sulpha drugs and currently used for the synthesis of juvenile hormone analogues3-5 which are further used as potential insecticides and pesticides. Utmost frequently working methods for the determination of these compounds hang on on the comparatively facile splitting of their S-Cl bond in hydrolysis kind reactions with water, bases, amines and hydroxylamine, where the chloride is ejected and sulphur leftovers hexavalent in sulphonic acid or their plagiaristic formed in these reactions. Diverse approaches have been conversed and used for the determination of sulphonyl chlorides.

Keywords: Sulphonyl Chlorides, Sulphinic Acids, Oxidimetric Titration, Polarographic Analysis, Benzyl Mercaptan Reduction

INTRODUCTION

Sulphonyl chlorides are equitably reactive compounds; they have therefore, been determined by multiplle chemical methods[6-9].

(i) ***Replacement reactions:*** The reagent embraces water, bases, amines and hydroxylamine.

$$RSO_2 - Cl + H_2O \rightarrow RSO_3H + HCl$$

$$RSO_2 - Cl + R'O^- \rightarrow RSO_2OR' + Cl^-$$

$$RSO_2 - Cl + 2R'NH_2 \rightarrow RSO_2NHR' + R'NH_3^+Cl^-$$

Seeman *et al*[10] determined p-acetylaminobenzene sulphonyl chloride as a significant intermediate in the preparation of sulphanilamides. Recently, Frehden and Petroianu[11-12] determined simple hydrolysable halides, including p-acetylaminobenzenesulphonyl chloride, in a comparable technique by means of water/pyridine substance. Ashworth and Winter[13] completed this reaction as the basis of titrimetric determination of sulphonyl chlorides.

$$R - Hal + S_2O_3^{-2} \rightarrow R\text{-}S_2O_3^- + Hal^-$$

(ii) ***Reduction Methods:*** These approaches are grounded on reduction of sulphur (VI) in sulphonyl chlorides to sulphur (IV) in sulphinates or sulphur (II) in sulphide ion and in some cases organic disulphides. Ashworth and Coworkers[14-15] were able to work out a direct titration technique for a succession of sulphonyl halides, using sodium sulphite as titrant.

$$R - SO_2X + 2e^- \rightarrow R\text{-}SO_2^- + X^- \quad (X = \text{Halogen})$$

(i) ***Spectrophotometric Methods:*** Simple spectrophotometric methods for determination of sulphonyl chlorides and carbonyl chlorides are projected by Siewinski[16]. Kuznetsov and Lyaufer[17] determined anthraquinone mono sulphonic acid by spectrophotometric titrimetery with barium salts in 50% acetone in the presence of nitchromazo

(iii) ***Polarographic Methods:*** Polarographic reduction of sulphonyl halides appears normally to be a 2-electron process, yielding sulphinates and halides[18-21]. However, Urabe and Yasukochi[22] planned diverse mechanisms under certain experimental situations:

$$R - SO_2Cl + 3H^+ + 3e^- \rightarrow \frac{1}{2}R\text{-}SO_2SR + HCl + H_2O$$

$$R - SO_2Cl + 5H^+ + 5e^- \rightarrow \frac{1}{2}R\text{-}SSR + HCl + 2H_2O$$

Virtually no polarographic work on sulphonyl halides has been analytically leaning.

(iv) ***Chromatographic Methods:*** An amalgamation of liquid phase chromatographic separation on silica gel and Infra-Red and emission spectroscopy have been used for the investigation of oil-soluble sulphonates. Kang *et al* [23] applied the reverse phase ion-pair chromatography for the parting of aromatic sulphonic acids on an alkyl altered silica. Nakada *et al*[24] have done the analysis of aromatic sulphonic acids and sulphonates by gas chromatography. Gas chromatographic analysis of numerous sulphonyl chlorides with derivatization has been defined recently by Tazerouti *et al*[25].

DETERMINATION OF SULPHONYL CHLORIDES

In the current work, the use of mercaptans has been defined for carrying about the reduction of hexavalent sulphur. The technique comprises in reacting each sulphonyl chloride with a mercaptan (benzyl mercaptan used in the current examination in dimethylformamide medium, thereby converting it to sulphinic acids. The additional mercaptan is masked with alkaline acrylonitrile to form cynoethylsulphide (which are non-ionizable) and sulphinic acids measured

$$R - SO_2Cl + 2R'SH \rightarrow R\text{-}SOOH + HCl + R'SSR'$$

by an oxidimetric method.

$$R - SH + CH_2 = CHCN \rightarrow RSCH_2CH_2CN$$

Ammonium hexanitratocerate (IV) (in dilute sulphuric acid) and lead (IV) acetate (in glacial acetic acid) have been found appropriate oxidants for the titrimetric determination of sulphinic acids and consequently of sulphonyl chlorides. The end points may be spotted visually or potentiometrically.

$$R-SOOH + H_2O + 2Ce^{+4} \rightarrow R\text{-}SO_2OH + 2H^+ + 2Ce^{+3}$$

$$R-SOOH + H_2O + Pb^{+4} \rightarrow R\text{-}SO_2OH + 2H^+ + Pb^{+2}$$

EXPERIMENTAL

(a) Preparation/source of compounds:

1. ***Sulphonyl chlorides:*** Benzene sulphonyl chloride was distilled before use.
2. ***Pyridine Perchlorate:*** The compound was prepared by mingling equimolar amounts of pyridine (A.R., Ranbaxy) and perchloric acid (Anal, R, BDH) in an ice chilled beaker with persistent stirring. A white compound separates out instantly.

(b) ***Preparation of Reagent solutions:*** Glacial acetic acid (BDH, AR) was refluxed with a slight potassium permanganate for near about two hours and fractionally distilled at 118°.

Dimethylformamide (BDH) was decontaminated via keeping it over Na_2CO_3 (AR) for 48 hours. The solvent was removed off, simply distilled and then finally fractionally distilled at 148.5° to 149.5° was gathered in coloured flasks.

K_2CS_3, potassium trithiocarbonate was made by technique of Deskin[26]. Saturated solution of potassium hydroxide in absolute alcohol was taken in a conical flask and saturated with hydrogen sulphide, followed by sluggish addition of carbon disulphide solution (in absolute alcohol), from dropping funnel with continuous stirring. The stirring was sustained for twenty minutes after this addition. The orange-coloured crystals of the compound were obtained. After that, the compounds were separated by filtration, cleaned with absolute alcohol, dehydrated and kept inside a vacuum desiccator. A known concentration solution of the compound was made by liquifying a little more than the designed quantity in twice distilled boiled water then standardized iodometrically by means of starch as chemical indicator.

Potassium iodate, 0.02N in water: 0.7133 g of potassium iodate (BDH, AR), dried at 160° were dissolved in distilled water and volume made to one litre.

Sodium thiosulphate, 0.05N in water: 2.40 g of sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$ (BDH, AR) were dissolved in boiled out distilled water and the volume made to one litre. The solution was standardized iodometrically using potassium iodate solution.

Iodine, 0.05N in Water was prepared and standardized as usual.

Ferrous ammonium sulphate, 0.04N in 1N H_2SO_4: 15.085 g of compound $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$ (BDH, AR) were liquified in 1N-sulphuric acid and the capacity made to one liter with the acid. Ammonium hexanitratocerate (IV), 0.04N in one normal Sulphuric acid had been prepared through liquifying a slight extra than the intended quantity of oxidant (Fluka., Switzerland) in 1N sulphuric acid then standardized via titration with requisite standard ferrous ammonium sulphate in the occurrence of dilute H_2SO_4 by means of ferroin as chemical indicator.

Pyridine perchlorate, 0.05M in dimethylformamide had been made by liquifying 0.223 g pyridine perchlorate in 25mL of dimethylformamide.

Lead (IV) acetate, 0.05N in glacial acetic acid: The compound was prepared by the technique pronounced by Grindley[27]. To a blend of acetic acid (225 mL) with acetic anhydride (85 mL) was added red lead (150 g) gradually and with dynamic shuddering. Subsequently reaction is exothermic, the rate of addition of red lead was controlled so that the temperature progressively fell and near the end of the reaction, the reaction mixture was heated to 60°. The clear solution so attained was permitted to cool when hefty measures of lead (IV) acetate precipitated. The compound was filtered under vacuum and splashed numerous times with acetic acid. It was further recrystallized from warm acetic acid. A solution of known concentration (standard one) was made through liquifying slightly extra than the requisite calculated amount of the oxidant in glacial acetic acid then made it standard one by iodometrically.

Indicator solution: Starch 1% aqueous solution.

Ferrous phenanthroline sulphate (ferroin), 0.01 N in water: 0.594 g of 1,10-phenanthroline monohydrate and 0.278 g of ferrous sulphate heptahydrate (BDH, AR) were liquified in 100mL of water. Diphenylamine: 0.1% solution in concentrated sulphuric acid.

Methyl Red: 0.1% in 60% alcohol.

Quinalizarin (1, 2, 5, 8-tetrahydroxy anthraquinone): 0.2% solution in glacial acetic acid.

PROCEDURE

A) Procedures based on their reduction with benzyl mercaptan followed by the titrimetric determination of subsequent reduction products viz. Sulphinic acids and/or HCl.

1. ***Determination of sulphinic acids:*** Oxidimetric determination with ammonium hexanitratocerate (IV) Aliquots of the dimethylformamide solutions of benzene sulphonyl chloride had been reserved in dehydrated titration containers, mixed with benzyl mercaptan (1 mL of 0.1 N in dimethylformamide) and the volume made to 5 mL with dimethylformamide. After 5 minutes, potassium hydroxide (1 mL of 0.2 M of water) and acrylonitrile (2mL of 0.5 N in dimethylformamide) were added. Finally, every liquid solution had been mixed through 30-35 mL, 1N H_2SO_4 then titrated visually and potentiometrically at room temperature (25°) against standard (0.04 N) ammonium hexanitratocerate (IV). In case of visual titrations, ferroin (1-2 droplets) was likewise added and the end point was seen through a strident colour alteration as of red to very light blue. However, in case of potentiometric titrations, a steep rise of potential had been noticed at the equivalence point. Potentiometric titration curves have been revealed in Figure 1. The results have been appended in Table I.

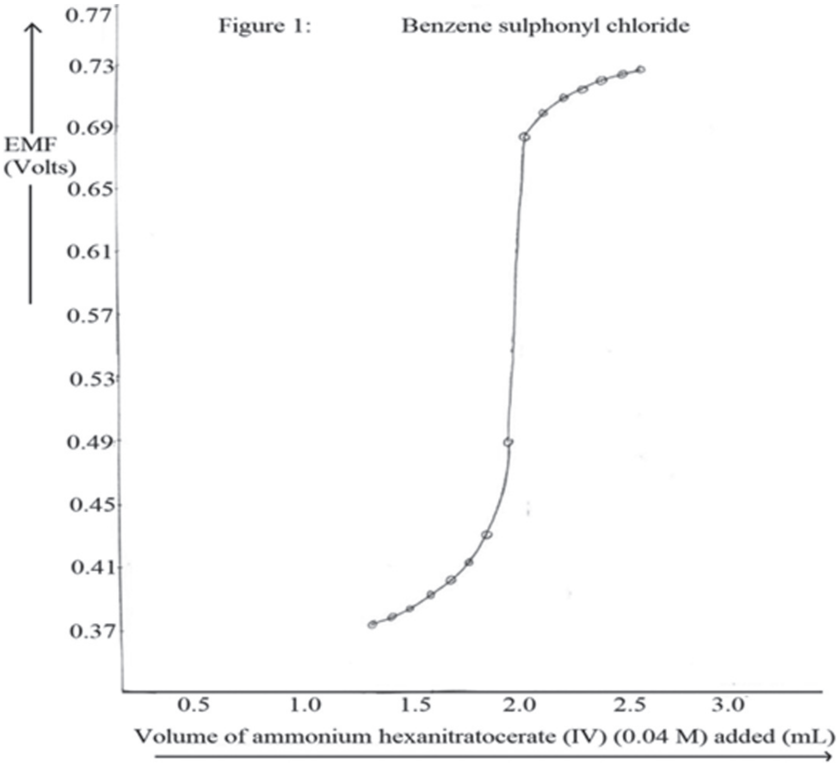

Table I: Determination of sulphonyl chloride: Reactionwith benzyl marcaptan followed by oxidimetric titration of resulting sulphinic acids with ammonium hexanitrato cerate (IV)

Sulphonyl Chloride	The values are mean of ten determinations with standard deviation (±)			
	Visual Procedure		Potentiometric Procedure	
	Amount found* mg	Amount found** mg	Amount found* mg	Amount found** mg
Benzene	3.04, 0.029	8.02, 0.046	3.07, 0.030	8.08, 0.059

* Quantity taken, 3 mg

** Quantity taken, 8 mg

(B) ***Oxidimetric determination with lead (IV) acetate:*** Aliquots of dimethylformamide solutions of each sulphonyl chloride had been reserved in dehydrated titration flasks, mixed with benzyl mercaptan (1 mL of 0.1 N in dimethylformamide) and the volume made to 5 mL with dimethylformamide. After minutes, potassium hydroxide (1 mL of 0.2 M in water) and acrylonitrile (2 mL of 0.5 M in dimethylformamide) were added. Lastly, each liquid solution was combined with 30-35 mL of glacial acetic acid and titrated visually and potentiometrically at room temperature (25^{o}) against standard (0.04 N) lead (IV) acetate. For visual titrations quinalizarin (1-2 drops) was also added; the completion of reaction i.e., end point was noticed by a steep colour variation from orange toward purple. Figure 2 indicated the profiles of potentiometric titrations. The results are presented in Table II.

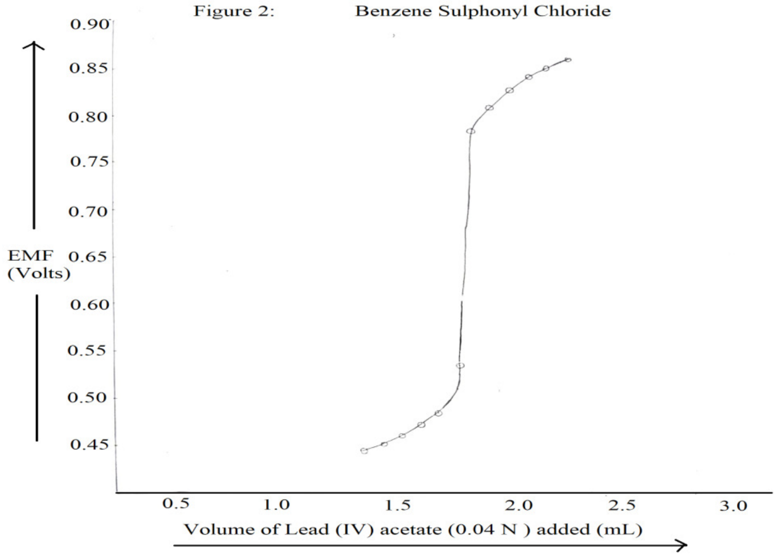
Figure 2: Benzene Sulphonyl Chloride

Table II: Determination of sulphonyl chloride reaction with benzyl marcaptan followed by oxidimetric titration of resulting sulphinic acids with lead (IV) acetate

Sulphonyl Chloride	The values are mean of ten determinations with standard deviation (±)			
	Visual Procedure		Potentiometric Procedure	
	Amount found* mg	Quantity found** mg	Quantity found* mg	Quantity found** mg
Benzene	3.94, 0.036	9.98, 0.047	4.01, 0.038	10.01, 0.052
* Quantity, 4 mg ** Quantity taken, 10 mg				

(2) Determination of Sulphinic acid and hydrochloric acid

A) ***Alkalimetric determination with potassium trithiocarbonate:*** Aliquots of the dimethylformamide solutions of each sulphonyl chloride had been reserved in dehydrated titration flasks, mixed with benzyl mercaptan (1 mL of 0.1 M in dimethylformamide) and the capacity made to 5 mL with dimethylformamide. After 5 minutes, potassium hydroxide (1 mL of 0.2 M in water) and acrylonitrile (2 ml of 0.5 M in dimethylformamide) were added. Lastly, individual liquid solution had been mixed with 30-35 mL of distilled water then titrated as above visually besides pH metrically at normal temperature (25^{o}) against standard (0.04 N) potassium trithiocarbonate. In case of visual titrations, the completion i.e., the end point had been noticed through yellow colour reported in the liquid solution by means of the initial droplet of the agent compound poured in extra amount. In pH titrations, a shrill increase in pH was detected at equivalence point. A succession of visual and pH metric titrations was executed with dissimilar quantities of each compound. The pH titration curves are shown in Figure 3. The results had been shown in Table III.

Table III: Determination of sulphonyl chloride: reaction with benzyl marcaptan followed by alkalimetric titration of resulting sulphinic acids and hydrochloric acid with potassium trithiocarbonate

Sulphonyl Chloride	The values are mean of ten determinations with standard deviation (±)			
	Visual Procedure		Potentiometric Procedure	
	Amount found* mg	Amount found** mg	Amount found* mg	Amount found** mg
Benzene	3.94, 0.038	11.02, 0.079	3.98, 0.039	11.04, 0.062
*Amount taken, 4 mg ** Amount taken, 11 mg				

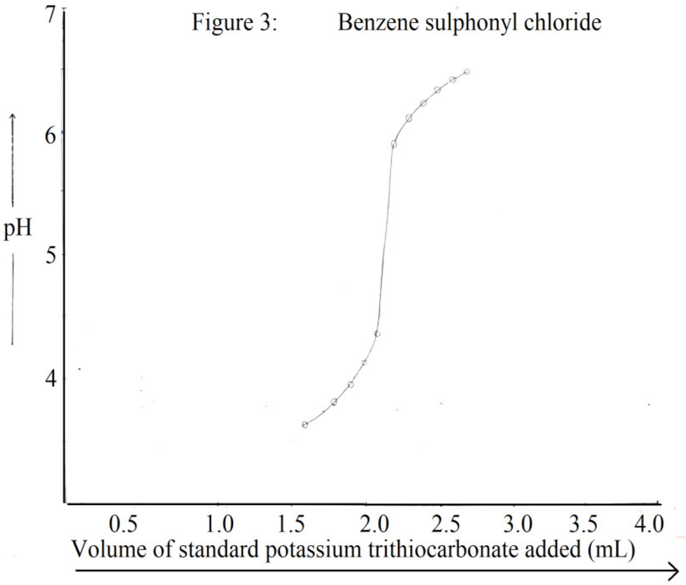

Figure 3: Benzene sulphonyl chloride

(B) Polarographic analysis

a) ***Measurements of half-wave potentials ($E^{1/2}$):*** Polarograms of Benzene sulphonyl chloride at known concentrations in distilled dimethylformamide medium in presence of pyridine perchlorate (0.05 M in dimethylformamide) at DME were documented. The universal technique for recording a polarogram was as follows:

A known measurement of supporting electrolyte solution (25 ml of 0.05 M pyridine perchlorate in dimethylformamide) was taken in a polarographic cell and essential connections were made. Liquefied oxygen was detached by passing a sluggish stream of clean nitrogen gas for about 5 minutes. The chart recording unit and emf sweep were started instantaneously. Later recording the polarogram of supporting electrolyte alone, the mercury reservoir was dropped and chart recording unit switched off. Then, aliquots in dimethylformamide of each compound were added in polarographic cell, de-aerated and polarograms recorded in the usual manner. Distinctive polarograms, one for each compound, are shown in Figure 4. In Table IV are listed the values of half wave potential of these compounds.

Table IV: Half wave potential of sulphonyl chlorides

Compound	$E^{1/2}$ in volts (vs. SCE)
Benzene sulphonyl chloride	-0.390

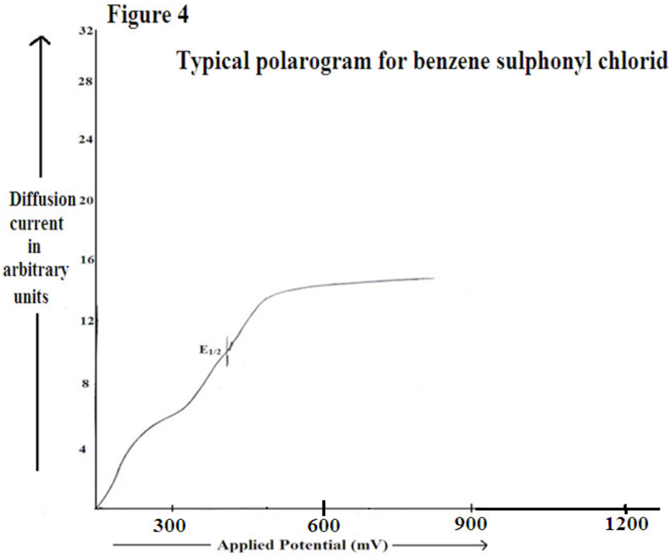

Figure 4

Typical polarogram for benzene sulphonyl chloride

b) ***Preparation of calibration graphs:*** Aliquots of solutions in dimethylformamide of benzene sulphonyl chloride was taken in the cell comprising pyridine perchlorate (25 ml of 0.05 M in dimethylformamide). Nitrogen gas was bubbled through the solution for 5 minutes besides polarograms were documented in the similar way as defined under universal technique. The standardized calibrated statistics of the benzene sulphonyl chloride has been given in Table V, the calibration data and their plots are shown in Figure 5-6. Outcomes of determination are given in Table VI.

Table V: Calibration data for benzene sulphonyl chloride Mass of mercury flowing / Sec (m) = 2.72 mg

Time for each drop (t) = 2.5 Sec				
Curve	Concentration of benzene sulphonyl chloride	Diffusion Current*		$I = id / Cm^{2/3} t^{1/6}$
	in µg / 25 m	In arbitrary units	In µ amp**	
A	35.4	10	1.1	0.014
B	53.1	17	1.7	0.014
C	70.8	23	2.4	0.015
D	88.5	28	2.8	0.014

Figure 5: Polarogram of pure benzene sulphonyl Chloride at know concentrations

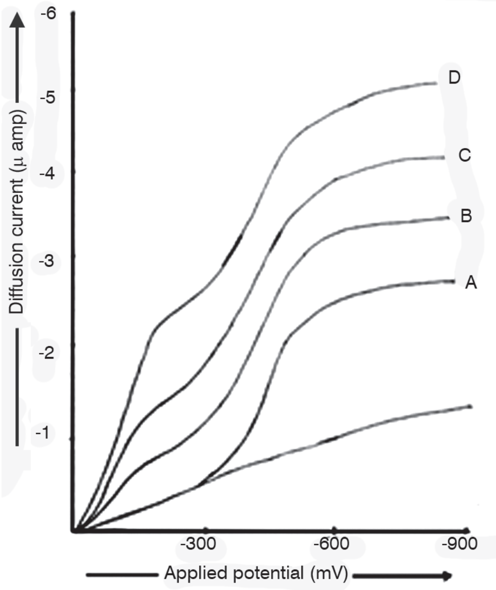

Figure 6: Calibration curve for pure benzene sulphonyl chloride

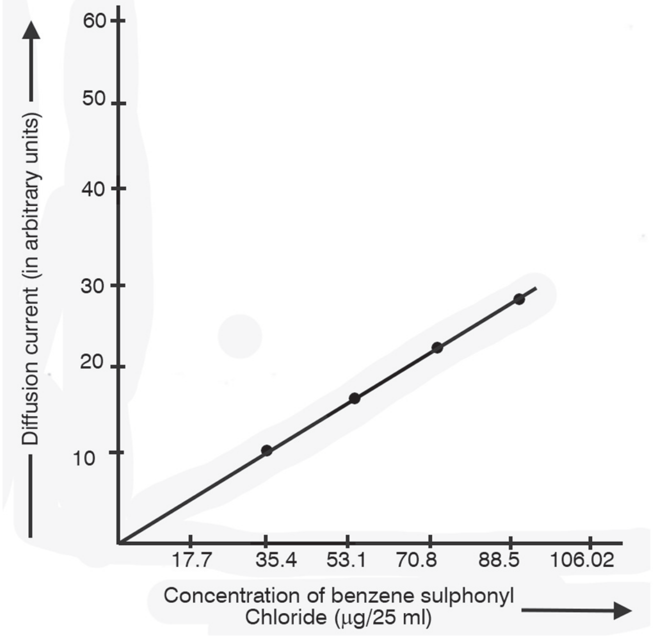

Table VI: Polarographic determination of benzene sulphonyl chloride

Amount taken*, µg	Amount found**, µg
25.0	25.3, 0.20
50.0	48.6, 0.42
75.0	75.6, 0.28
100.0	99.4, 0.42

* Corrected for residual current

** Average diffusion current in ì amp during the life of one drop

** The values stand mean of five determinations through standard deviation (±).

c) Polarograms of pure benzene sulphonyl chloride at a fixed concentration but at various heights of mercury column were recorded in the usual way. They showed that diffusion current bears a simple linear relationship with the square root of altitude of mercury column. The values of $id/h_{Hg}^{1/2}$ were found to be fairly constant (Table VII).

Table VII: The effect of height of Hg column on diffusion current

Concentration of compound taken = 20 µg / ml		
Height of mercury column in cm	$h^{1/2}$	$id / h^{1/2}$
		Benzene sulphonyl chloride
75.00	8.66	0.25
65.00	8.06	0.25
55.00	7.42	0.26
45.00	6.71	0.25
35.00	5.92	0.26

RESULT AND DISCUSSION

Sulphonyl chlorides are compounds of having economical, synthetic and analytical importance. Subsequently, their determination is of countless future scope and value. These compounds can be quantitatively reduced to the equivalent sulphinic acids and the later effectively determined oxidimetrically with cerium (IV) (in 1N-sulphuric acid) or lead (IV) (in glacial acetic acid) visually and potentiometrically, has been made the foundation of modest titrimetric methods for the determination of sulphonyl chlorides. The remaining mercaptan is made unreactive by masking it with alkaline acrylonitrile. The determination of sulphonyl chlorides has also been accomplished by titrating sulphinic acid and HCL, formed in their reaction with benzyl mercaptan, alkalimetrically with potassium trithiocarbonate visually or pH metrically.

Cobalt (II) reacts effortlessly and quantitatively with mercaptans to form brown coloured tetramarcaptocobaltate (II) complex in dimethylformamide-acetonitrile media. This reflection has been made use of in developing a photometric titrimetric technique for the determination of sulphonyl chlorides by titrating excess mercaptan with cobalt (II) at 475 nm.

Sulphonyl chlorides are reduced polarographically at dropping mercury electrode. This has been made the foundation of their determination by polarographic methods. The determination has been carried out in dimethylformamide solvent which acted as medium in the occurrence of pyridine perchlorate (supportive / subsidiary electrolyte) at the DME. The half-wave potentials have been noticed to be -0.390 V versus SCE in respect of benzene sulphonyl chloride. The reduction of these compounds is diffusion controlled. Since the plot of diffusion current versus the concentration of benzene sulphonyl chloride is linear and the wave is well defined, the polarographic reduction has been used for the quantitative determination of these compounds.

The titrimetric and polarographic procedures for the determination of sulphonyl chlorides are suitable and consistent and are suggested for their repetitive analysis.

REFERENCES

1. Olivannau, M.S. and Nayaudamma, Y; J. Sci. Ind. Res., 1969, 28, 293.
2. Skrypnik, Y.G. and Bezrodngi, V. P., Acad. Sci., Ukrainen, USSR, 1982, 901N31/08; Anal., Abstr., 1982, 97, 9.

3. R.K.Mahajan, Ved Parkash Patial and Pamita Sharma, Ind. J. Chem. 1998, 15, 1 & 2, 51-54.
4. R. K. Mahajan and Ved Parkash Patial, Nat. Acad. Sci. India, 72A, 2002, 287.
5. V. P. Patial and Rajnish Dewan, Shodh Shree, 2012, 3, 49-55.
6. Suter, C., "The organic Chemistry of Sulphur", Wiley and Sons, New York, 1943.
7. Karchmer J. H., "Analytical chemistry of sulphur and its compounds", Part II. Wiley Intersciences, Newyork, 1972.
8. Ashworth M. R. F., "The determination of sulphur containing groups", Vol. I and II, Academic Press, Newyork, 1972.
9. Reid E. E., "Organic chemistry of Bivalent Sulphur", Vol. III, Chemical Publishing Comp., NewYork, 1960.
10. Seaman, W., Norton A. R., Woods, J. T. and Massad, E. A. Ind. Eng. Chem., Anal Ect. 1944, 16, 517.
11. Frehden, O. and Petroianu, S., Rev. Chem. Bucharest, 1965, 16, 223.
12. Frehden, O. and Petroianu, S., Z. Anal Chem.., 1968, 220, 379.
13. Ashworth, M. R. F. and Winter, M., Anal, Chem. Acta, 1963, 29, 75.
14. Ashworth, M. R. F., Walisch, W. and Kronz-Dienhart, G., Anal., Chim. Acta, 1959, 20, 96.
15. Walisch, W, Hertel, D. F. and Ashworth, M. R. F., Chim, Anal. Paris, 1961, 43, 234.
16. Siewinski, M., Kuropatwa, M., Szewezauk., A., Anal. Chem. 1984, 56 (14), 2882-4 (Eng.).
17. Kuznetsov, V. V. and Lyaufer, M. S., Zh. Anal. Khim., 1980, 35 (4) 747-52 (Russ.) (Chem. Abstr. 1980, 93, 142344 J).
18. Mairanovskii, S. G. and Neiman, M. B. Dokl. Akad. Nauk- USSR, 1951, 79, 85.
19. Horner, L. and Nickel, H., Chem. Ber, 1956, 89, 1681.
20. Cernak J. and Blazej A., Chem., Zvesti, 1962, 16, 276.
21. Kovbuz, M. A., Kachanko, I. E., Popova, L. Z. and Vizgert, R. V., Zh. Obshch. Khim., 1968, 38, 1455.
22. Urabe, N. and Yasukochi, K., Denki Kagaku, 1956, 24, 360 (Chem. Abstr. 51, 14447).
23. Kang, S. W. Oh, H. B., Lec., S. S., Taehaff Hwahakhochi, 1986, 30 (2) 244-50 (Korean).
24. Nakada, M., Uzawa, A., Fukush, S., Tomita, H., Hirota, M. Nippon Kagakn, 1984, 728-31 (Japan).
25. Tazerouti, A. Rahal, S; Soumillion J. P. (Inst. Chim; USTHB, Algiers, Algeria) J. Chromatogr. 1992, 596 (1), 132-7 (Eng.).
26. Deskin, W. A., J., Amer. Chem. SOC. 1958, 80, 5680-82.
27. Grindley, D. N., " An advanced course in Practical Inorganic chemistry ", Butterworths, London, 1964, p. 79.