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ORIGINAL ARTICLE

DETERMINATION OF SOME SULPHONYL CHLORIDES-I

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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 impregnation[1]. Sulphonyl chlorides support as appreciated substances in certification and determination of primary and secondary amines and phenols[2]. 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 analogues[3-5] 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, Sulphonamide.

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INTRODUCTION

Sulphonyl chlorides are fairly reactive compounds; they have therefore been determined by variety of chemical methods[6-9].

(i) ***Replacement reactions:*** The reagent includes 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-acetyl aminobenzene sulphonyl chloride as an important intermediate in the preparation of sulphanilamides. More recently, Frehden and Petroianu[11-12] determined easily hydrolysable halides, including p-acetylaminobenzenesulphonyl chloride, in a similar procedure using water/pyridine reagent. Ashworth and Winter[13] made 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 methods are based 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 method for a series of sulphonyl halides, using sodium sulphite as titrant.

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

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

(iv) ***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] proposed different mechanisms under certain experimental conditions:

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

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

Practically no polarographic work on sulphonyl halides has been analytically orientated.

(v) ***Chromatographic Methods:*** A combination of liquid phase chromatographic separation on silica gel and Infra-Red and emission spectroscopy has been used for the analysis of oil-soluble sulphonates. Kang et al [23] applied the reverse phase ion-pair chromatography for the separation of aromatic sulphonic acids on an alkyl modified silica. Nakada et al[24] have done the analysis of aromatic sulphonic acids and sulphonates by gas chromatography. Gas chromatographic analysis of several sulphonyl chlorides with derivatisation has been described recently by Tazerouti et al[25].

DETERMINATION OF SULPHONYL CHLORIDES

In the present work, the use of mercaptans has been described for bringing about the reduction of hexavalent sulphur. The method consists in reacting each sulphonyl chloride with a mercaptan (benzyl mercaptan used in the present investigation) in dimethylformamide medium, thereby converting it to sulphinic acids. The excess mercaptan is masked with alkaline acrylonitrile to form

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

Cynoethylsulphide (which are non-ionizable) and sulphinic acids measured by an oxidimetric method.

$$R - SH + CH_2 = CH.CN \rightarrow RSCH_2CH_2CN$$

Ammonium hexanitratocerate (IV) (in dilute sulphuric acid) and lead (IV) acetate (in glacial acetic acid) have been found suitable oxidants for the titrimetric determination of sulphinic acids and consequently of sulphonyl chlorides. The end-points may be detected 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, p-toluene and methane sulphonyl chlorides were distilled before use.
2. ***Pyridine Perchlorate:*** The compound was prepared by mixing equimolar quantities of pyridine (A.R., Ranbaxy) and perchloric acid (Anal, R, BDH) in an ice cooled beaker with constant stirring. A white compound separates out immediately.

(b) ***Preparation of Reagent solutions:*** Glacial acetic acid (BDH, AR) was refluxed with a little potassium permanganate for about 2 hours and fractionally distilled at 118°.

Dimethylformamide (BDH) was purified by storing it over sodium carbonate (AR) for 2 days. The solvent was decanted off, distilled and fraction distilling at 148.5° to 149.5° was collected in coloured bottles.

Potassium trithiocarbonate (K_2CS_3) was prepared by method of Deskin[26]. Saturated solution of potassium hydroxide in absolute alcohol was taken in a conical flask and saturated with hydrogen sulphide, followed by slow addition of carbon disulphide solution (in absolute alcohol), from dropping funnel with constant stirring. The stirring was continued for 20 minutes after this addition. The orange coloured crystals of the compound separated out. The compound was removed by filtration, washed with absolute alcohol, dried and kept in a vacuum desiccator. A standard solution of the compound was prepared by dissolving a little more than the calculated amount in doubly distilled boiled water and standardized iodometrically using starch indicator.

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

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 liter. 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: 15.085g of compound $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$ (BDH, AR) were dissolved in 1N-sulphuric acid and the volume made to one liter with the acid.

Ammonium hexanitratocerate (IV), 0.04N in 1N Sulphuric acid was prepared by dissolving a little more than the calculated amount of oxidant (Fluka., Switzerlad) in 1N sulphuric acid and standardized by titration with standard ferrous ammonium sulphate in the presence of dilute sulphuric acid using ferroin indicator.

Pyridine perchlorate, 0.05M in dimethylformamide was prepared by dissolving 0.223 g of pyridine perchlorate in 25ml of dimethylformamide.

Lead (IV) acetate, 0.05N in glacial acetic acid: The compound was prepared by the method described by Grindley[27]. To a mixture of acetic acid (225 mL) and acetic anhydride (85 mL) was added red lead (150 g) slowly and with vigorous shaking. Since reaction is exothermic, the rate of addition of red lead was regulated so that the temperature gradually fell and towards the end of the reaction, the reaction mixture was heated to 60°C. The clear solution so obtained was allowed to cool when large quantities of lead (IV) acetate precipitated. The compound was filtered under vacuum and washed several times with acetic acid. It was further recrystallized from hot acetic acid. A standard solution was prepared by dissolving a little more than the calculated amount of the oxidant in glacial acetic acid and standardized iodometrically.

Indicator solution: Starch 1% aqueous solution.

Ferrous phenanthroline sulphate (ferroin), 0.01 N in water: 0.594g of 1,10-phenanthroline monohydrate and 0.278g of ferrous sulphate heptahydrate (BDH, AR) were dissolved in 100 mL 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.

PROCEDURES:

Determination of Sulphonyl Chlorides:

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

1. ***Determination of sulphinic acids:***

A) Oxidimetric determination with ammonium hexanitrato cerate (IV): Aliquots of the dimethylformamide solutions of benzene sulphonyl chloride were taken in dry titration vessels, 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 in water) and acrylonitrile (2mL of 0.5 N in dimethylformamide) were added. Finally, each solution was mixed with 30-35 ml of 1N sulphuric acid and titrated visually and potentiometrically at room temperature (25^{o}C) against standard (0.04N) ammonium hexanitratocerate (IV). For visual titrations, ferroin (1-2 drops) was also added; the end point was marked by a sharp colour change from red to very light blue. In potentiometric titrations, a sharp rise in potential was observed at the equivalence point. The potentiometric titration curves are shown in Figure 1. The results are given in Table I.

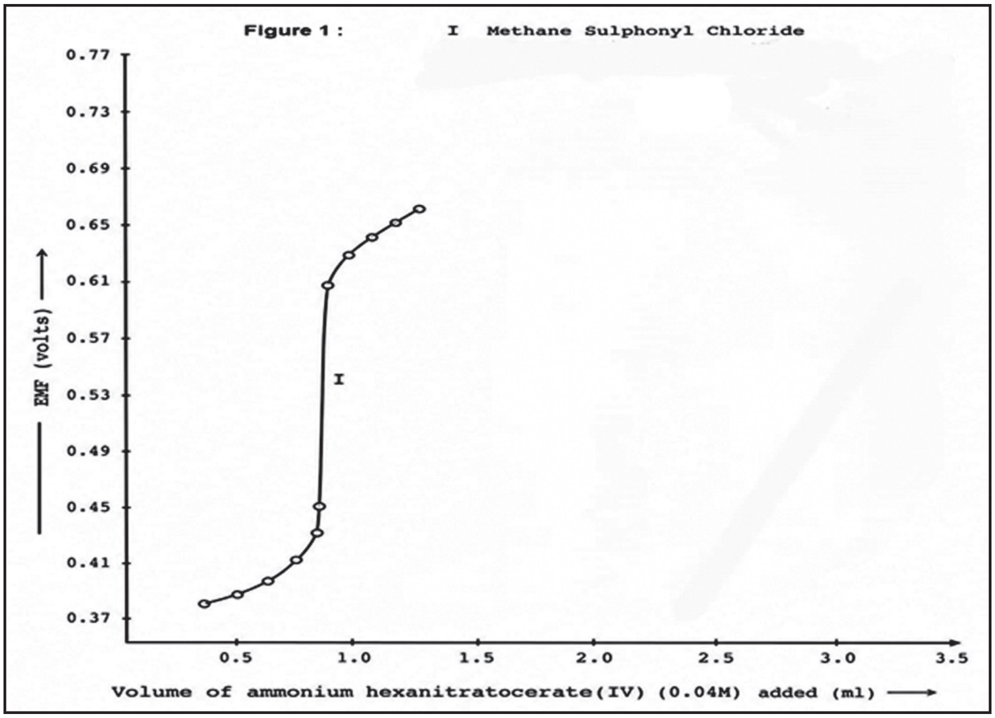


Table I: Determination of sulphonyl chloride: Reaction with benzyl marcaptan followed by oxidimetric titration of resulting sulphinic acids with ammonium hexanitrato cerate (IV)

Sulphonyl Chloride	**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**
Methane	3.02, 0.028	7.98, 0.045	3.04, 0.025	8.04, 0.063

*Amount taken, 3 mg

** Amount taken, 8 mg

(B) ***Oxidimetric determination with lead (IV) acetate:*** Aliquots of dimethylformamide solutions of each sulphonyl chloride were taken in dry titration vessels, 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 in water) and acrylonitrile (2 ml of 0.5 M in dimethylformamide) were added. Finally, each solution was mixed with 30-35 ml of glacial acetic acid and titrated visually and potentiometrically at room temperature (25ºC) against standard (0.04 N) lead (IV) acetate. For visual titrations quinalizarin (1-2 drops) was also added; the end point was marked by a sharp colour change from orange to purple. In Figure 2 are shown the profiles of potentiometric titrations. The results are given in Table II.

Figure: 2

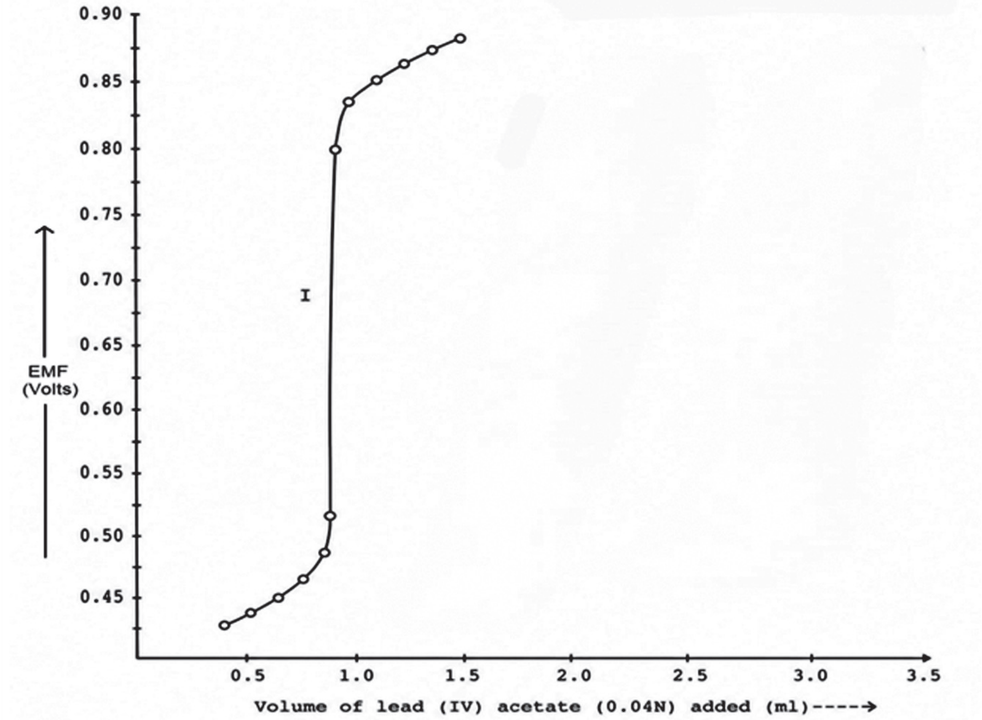


Table II: Determination of sulphonyl chloride: Reaction with benzyl marcaptan followed by oxidimetric titration of resulting sulphinic acids with lead (IV) acetate

Sulphonyl Chloride	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
Methane	3.96, 0.040	9.94, 0.043	3.98, 0.040	9.98, 0.045

*Amount *Amount taken, 4 mg

** Amount 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 were taken in dry titration vessels, mixed with benzyl mercaptan (1 ml of 0.1 M in dimethylformamide) and the volume 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. Finally, each solution was mixed with 30-35 ml of distilled water and titrated visually and pH metrically at room temperature (25^{o}C) against standard (0.04 N) potassium trithiocarbonate. In visual titrations, the end point was marked by yellow colour imparted to the solution by the first drop of the reagent added in excess. In pH titrations, a sharp rise in pH was observed at equivalence point. A series of visual and pH metric titrations was performed with different amounts of each compound. The pH titration curves are shown in Figure 3. The results are given in Table III.

Figure: 3

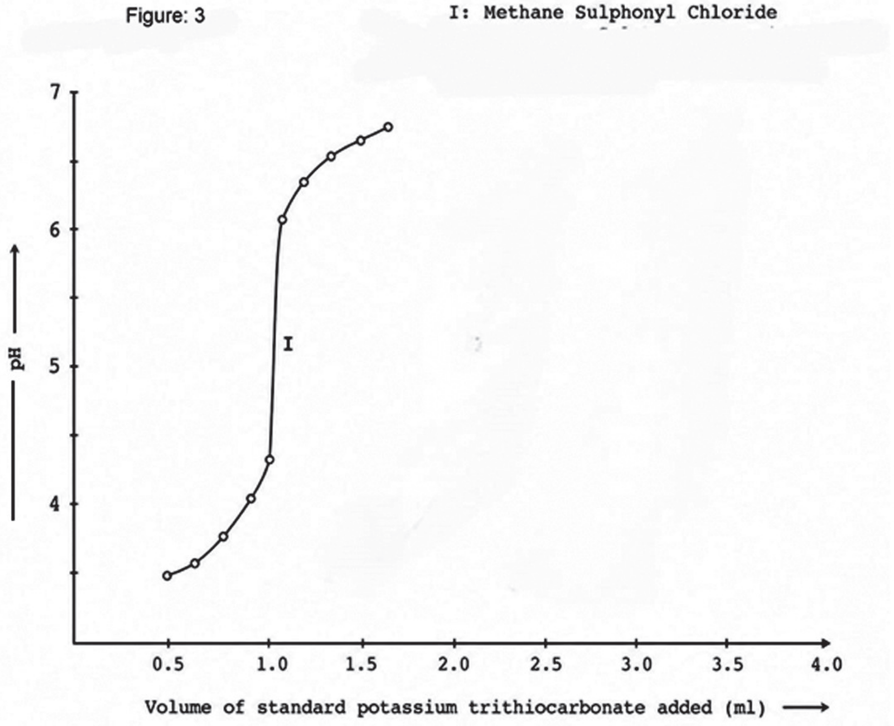


Table III: Determination of sulphonyl chloride: Reaction with benzyl marcaptan followed by alkalimetric titration of resulting sulphinic acids and hydrochloric acid with potassium trithiocarbonate

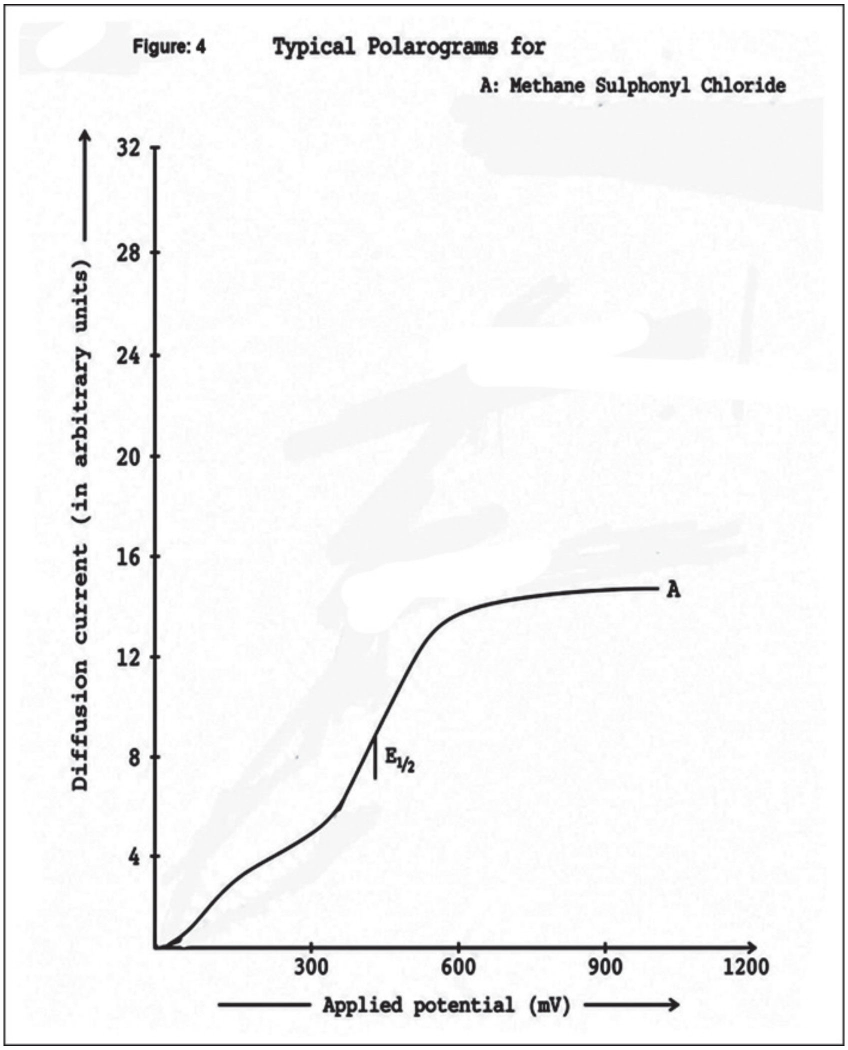
Sulphonyl Chloride	**Values are mean of ten determinations with standard deviation (±)**			
	Visual Procedure		**Potentiometric Procedure**	
	Amount found* mg	**Amount found** mg**	**Amount found* mg**	**Amount found** mg**
Methane	3.98, 0.040	10.96, 0.068	4.00, 0.035	11.02, 0.059

* Amount taken, 4 mg

**Amount taken, 11 mg

(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 recorded. The general procedure for recording a polarogram was as follows:



A known volume of supporting electrolyte solution (25 mL of 0.05 M pyridine perchlorate in dimethylformamide) was taken in a polarographic cell and necessary connections were made. Dissolved oxygen was removed by passing a slow stream of pure nitrogen gas for about 5 minutes. The chart recording unit and emf sweep were started simultaneously. After recording the polarogram of supporting electrolyte alone, the mercury reservoir was lowered and chart recording unit switched off. Then, aliquots in dimethylformamide of each compound were added in polarographic cell, deareated and polarograms recorded in the usual manner. Typical 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	E1/2 in volts (vs. SCE)
Methane sulphonyl chloride	-0.420

b) **Preparation of calibration graphs:** Aliquots of solutions in dimethylformamide of benzene sulphonyl chloride was taken in the cell containing pyridine perchlorate (25 ml of 0.05 M in dimethylformamide). Nitrogen gas was bubbled through the solution for 5 minutes and polarograms were recorded in the same manner as described under general procedure. The calibration data of the benzene sulphonyl chloride is given in Table V, the calibration data and their plots are shown in Figure 5-6. Results of determination are given in Table VI.

Figure 5 : Polarograms of pure methane sulphonyl chloride at known concentrations

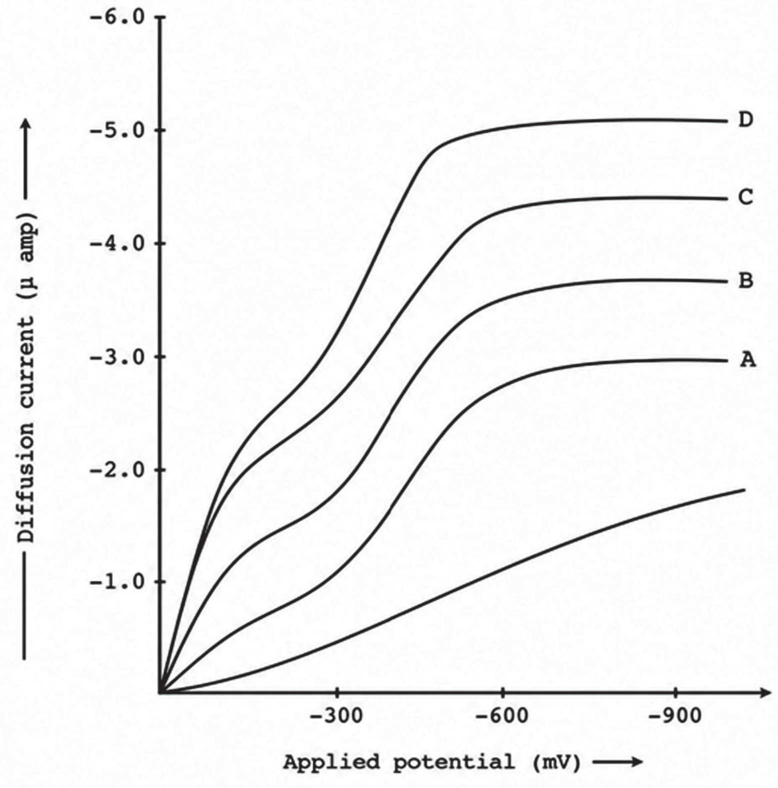


Table V: Calibration data for Methane sulphonyl chloride

Mass of mercury flowing / Sec (m) = 2.72 mg Time for each drop (t) = 2.5 Sec

Curve	Concentration of Methane sulphonyl chloride	Diffusion Current*		I = id / $Cm^{2/3} t^{1/6}$
	In µg / 25 ml	In arbitrary units	In µ amp**	
A	22.8	15	1.5	0.029
B	34.2	23	2.3	0.028
C	45.6	30	3.0	0.029
D	57.0	37	3.7	0.028

*Corrected for residual current

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

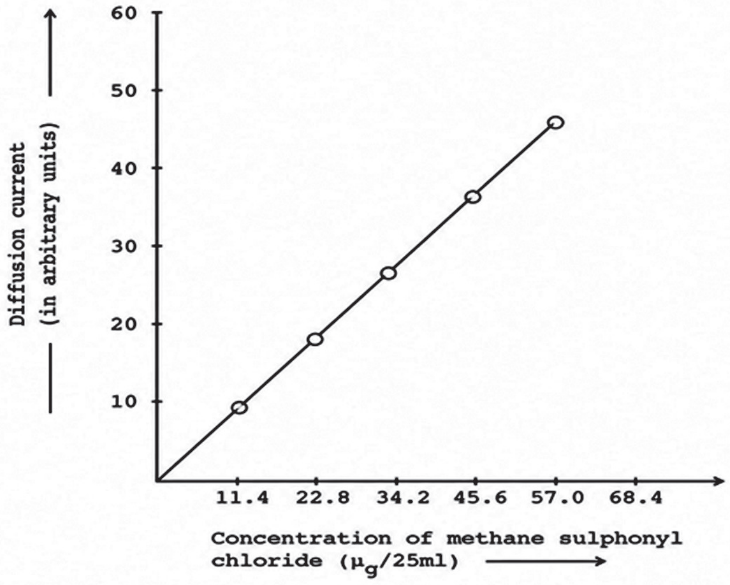


Figure 6 : Calibration curve for pure methane sulphonyl chloride

Table VI: Polarographic determination of Methane sulphonyl chloride

Amount taken, µg	Amount found**, µg
25.0	24.9, 0.19
50.0	50.5, 0.34
75.0	74.3, 0.32
100.0	99.6, 0.30

** Values are mean of five determinations with standard deviation (±).

c) Polarograms of pure sulphonyl chlorides 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 height of mercury column. A typical curve showing linear relationship between id and $h_{Hg}{}^{1/2}$ for sulphonyl chlorides represented in Figure. The values of $id/h_{Hg}{}^{1/2}$ were found to be fairly constant (Table VII).

Table VII: Effect of height of mercury column on diffusion current

Concentration of compound taken = 20 µg / ml		
Height of mercury column in cm	**$h^{1/2}$**	**$id / h^{1/2}$**
		Methane sulphonyl chloride
75.00	8.66	0.42
65.00	8.06	0.42
55.00	7.42	0.41
45.00	6.71	0.42
35.00	5.92	0.41

SUMMARY

Sulphonyl chlorides are compounds of commercial, synthetic and analytical importance. Consequently, their determination is of great scope and value. That these compounds can be quantitatively reduced to the corresponding sulphinic acids and the later successfully determined oxidimetrically with cerium (IV) (in 1n-sulphuric acid) or lead (IV) (in glacial acetic acid) visually and potentiometrically, has been made the basis of simple titrimetric methods for the determination of sulphonyl chlorides. The residual marcaptan is made unreactive by masking it with alkaline acrylonitrile.

The determination of sulphonyl chlorides has also been accomplished by titrating sulphinic acid and hydrochloric acid, formed in their reaction with benzyl marcaptan , alkalimetrically with potassium trithiocarbonate visually or pH metrically.

Cobalt (II) reacts smoothly and quantitatively with marcaptans to form brown coloured tetramarcaptocobaltate (II) complex in dimethylformamide-acetonitrile media. This observation has been made use of in evolving a photometric titrimetric procedure for the determination of sulphonyl chlorides by titrating excess marcaptan with cobalt (II) at 475 nm.

Sulphonyl chlorides are reduced polarographically at dropping mercury electrode. This has been made the basis of their determination by polarographic methods. The determination has been carried out in dimethylformamide medium in the presence of pyridine perchlorate (supporting electrolyte) at the DME. The half-wave potentials have been found to be -0.420 v, -0.390 v and -0.450 v versus SCE in respect of methane sulphonyl chloride and p-toluene sulphonyl chloride. The reduction of these compounds is diffusion controlled. Since the plot of diffusion current versus the concentration of each of sulphonyl chloride is linear and the wave is well defined, the polarographic reduction has been used for the quantitative determination of these compounds.

The proposed titrimetric and polarographic methods for the determination of sulphonyl chlorides are convenient and reliable and are recommended for their routine 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, pp. 79.