

Sulfide ion Selective Method of Analysis of Sulfurated Hydrogen in Alkaline Smoked Cigarette Solution

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ABSTRACT

Sulfurated hydrogen commonly called hydrogen sulfide (H_2S) is a clear, colorless, extremely toxic gas that has a rotten egg smell at low concentration. The human nose can detect H_2S at concentrations below 100 parts per billion (ppb). It is found least amount in cigarette smoke that has been the subject of analysis for many analytical chemists. This gases is soluble in alkaline medium and gives free sulfide (S^{2-}) ions. Sulfide ion concentration in cigarette smoke solution is found in the range of detection limit of lab made Silver- silver sulfide (Ag/Ag_2S) ion selective electrode (ISE). This project has designed to investigate the amount hydrogen sulfide as a free sulfide (S^{2-}) ion in cigarette smoke solution. Silver-silver sulfide ion selective electrode (Ag/Ag_2S ISE) and Silver-silver chloride ($Ag/AgCl$) reference electrode are prepared in the lab for determination. Detail protocol of standard addition method with modified Grant's plot is applied for estimation. Different brand of cigarette samples were collected from different area of Pokhara valley and analyzed. The average amount of H_2S per stick of cigarette smoke is found to vary from 0.0453 mg to 0.0573 mg in different brands. Among them sample no SA-5 shows 0.0453mg per stick of cigarette. This result is minimum in compare to other brands. Similarly, sample no SA- 7 have found 0.0573mg per stick which is higher in compare to other brands.

Key words: Cigarette smoke, hydrogen sulfide, ion selective electrode, standard addition method, Grant's plot method,

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INTRODUCTION

In ancient time, tobacco was smoked only by natives of America, but subsequently it was brought to Europe in the mid-16th century, than after smoking habit become wide spread all over the world.¹ The first cigarette factory was established in Havana in 1853 and that was set up in New Jersey of USA in 1919.² At present, not only in developed country but also in underdeveloped country like Nepal, cigarette smoking habit has been common needs of smokers. People smoked cigarette and different tobacco bearing products for pleasurable experience.³ Moreover, it may provide physiological and psychological sensation. But, at present, tobacco smoking is one of the major health problems in the world. In different countries of the world, young people misused cigarette by mixing different narcotic and sedatives substances like opium, morphine, heroine, smack and ganja with tobacco of cigarette for smoking. They know smoking habits and overused of narcotic substances can seriously damage health. Despite this, they continue smoking. The practice of printing "cigarette smoking can cause lungs cancer" and 'smoking is injurious to health' in each packet of has not been effective to discourage cigarette smoking habit. Analysis of tobacco and smoke is greatly stimulated by the smoking and health relationship. Widespread research

has been carried out for the isolation and identification of toxic, carcinogenic and many more substances of cigarette smoke in different research laboratory of the world.⁴ More than 2500 constituents in tobacco leaf and more than 3,000 components in tobacco smoke have been reported by different researchers.⁵ Cigarette smoke has been intensively studied for appropriate health effects. More than forty eight of its components are found to be toxic and carcinogenic.⁶ Hydrogen sulfide is not a carcinogenic agent but it is one of the highly toxic chemical compounds found in cigarette smoke.¹ Researcher has been isolated various sulphur bearing compounds from cigarette smoke.⁷ Different authors have reported the existence of hydrogen sulfide in cigarette smokes.⁸

Hydrogen sulfide is a colorless, highly offensive and rotten egg odor gas. In alkaline medium, it behaves as like weak dibasic acid, which ionizes in two steps to produce hydro-sulfide (HS^-) ion and sulfide(S^{2-}) ions.⁹ Due to this reason its analysis is possible in the alkaline medium. The reported threshold odor of this gas is 25ppb/0.035mg/m³.¹⁰ But approximately 100 ppm concentration in air, it may cause the loss of olfactory sensation and giving a false sense of safe absence of the gas. At levels between 500 to 1000 ppm critical intoxication is associated with symptoms of sudden fatigue, headache, vomiting, hypertension, mental

disturbances and many more respiratory problems. In our country, more than seven billion sticks of cigarette are manufactured annually by different cigarette factories.¹¹ In Nepal, cigarette smoking habits of female is higher rank in compare to male especially in rural area. But in urban metropolitan area, due to the influence of western culture like hippy fashion and nuclear life style, the smoking habit is gradually stabilizing as a fashionable trend among the gender. Although the cigarette smoke contains many toxic chemicals, the main objective of this project is to determine the exact amount of H₂S per stick of different brand of cigarettes available in local markets of Pokhara valley.

MATERIAL AND METHODS

Chemicals and Reagents

Chemicals and reagents (AgNO₃, Ag₂SO₄, NaOH, FeCl₃, KCl, Na₂S₂O₃) were purchased from Merck Chemicals (India) through local supplier. All chemicals and reagents used were of analytical grade and used without further purification.

Cigarette samples

All the cigarettes (Table-1) were collected from different area of Pokhara sub metropolitan randomly. Cigarette samples were kept in the Analytical Laboratory of School of Health and Allied Sciences, Pokhara University, Lekhnath, Nepal.

Preparation of Silver Sulfide (Ag₂S) Ion selective electrode (ISE)

The silver sulfide ion selective electrode was prepared according to the method designed by Yadav and Pradhananga, 1995¹² with some modifications. In brief, in 100 mL of saturated solution of silver sulfate (Ag₂SO₄), equal volumes of saturated solution of sodium sulfide (Na₂S) were mixed for complete precipitation of silver sulfide (Ag₂S). Precipitate so obtained was filtered & washed several times by distilled water till the precipitate was free from any soluble impurities. Finally it was washed with acetone and dried in an air oven at 120°C for six hour. The precipitate was pulverized in agate mortar. About 1.5gm of precipitate was transferred into KBr mold and was evacuated for 5 min and then pressed under vacuum for 15 min by applying a pressure of 1 GPa (i.e. 10 tons/cm²) in IR pellet pressing machine. The pellet was removed carefully from the mold and silver paste was carefully applied on one side. The pellet was then mounted in a polypropylene tube with the help of Araldite and back contact was made with silver epoxy conducting paint with silver disk in which a copper wire was soldered. When Araldite was completely dried, the electrode was polished in an emery paper and finally in a Bolton cloth to a mirror finished.

Preparation of Ag/AgCl reference electrode

The laboratory made silver-silver chloride reference electrode was prepared according to the method designed by Bailery PL, 1980¹³ with some modifications. In brief,

the electrode was prepared by immersing approx 4 cm long pure and dry silver wire into a 5M ferric chloride solution till the wire changes to dark grey color due to deposition of silver chloride covering over the surface of silver wire. After washing and drying one of the free ends of this wire was connected to copper wire through solder for electric contact. It was then fixed in a 3ml disposal plunger. On the other hand 1.0 gm silver chloride powder and 0.5 gm of potato agar were mixed in a 50 ml saturated solution of KCl and the solution was boiled for few minutes. It was then allowed to cool for some time & then transfer to 5ml disposal plunger. Previously prepared electrode was then adjusted in this plunger and allowed to cool for twenty minutes for setting. This electrode was coupled with sulfide ISE for the potentiometric measurement of emf of standard and test solutions.

Preparation of cigarette smoke solution

The cigarette smoke solution was prepared according to the method designed by Tandukar S, 2000 with some modifications.¹⁴ In brief, 50 mL of 0.1M NaOH solution was taken in a gas washing bottle. A cigarette was attached to the inlet of gas washing bottle and the outlet was connected to a suction pump operated by water supply from a tap. The water supply was turned on and cigarette was lit. The smoke bubbles were collected in alkali solution via connection pipe. The water tap was so adjusted that it takes about 5-10 minutes to completely puff off the cigarette. The smoke solution was left for 5minutes so that the foggy smoke clears off. The resulting solution contained H₂S in the form of hydrosulfide (HS⁻). Same technique was applied to prepared cigarette smoke solution for different brands.

Standardization of hydrosulfide ion (HS⁻) test solution

For the standardization of hydrosulfide ion (HS⁻) of test solution the protocol prescribed by D.W. Hatchett et al. 2000¹⁵ was applied.

Data Collection Method

The standard addition method was preferred rather than direct potentiometry and potentiometric titration method if the concentration of determinant is very low¹⁴. To check the applicability of this method, 40 ml of 1x10⁻⁵M Na₂S solution were mixed in 0.1M NaOH solution taken in a flask and 1 mL of standard 2x 10⁻⁴M Na₂S solution in 0.1M NaOH was mixed from burette at a time till there was an appreciable change in emf for each addition of Na₂S standard solution. The data were then plotted according to modified Gran's plot as shown in figure 1 of result. Similar process was repeated for determining the concentration of H₂S in cigarette smoke solution. In brief, for this 50 mL of cigarette solution was taken in a titrating flask and 1 ml of standard 2x 10⁻⁴M Na₂S solution was added from burette at a time till there were appreciable changes in emf after each addition of standard reagent. All together nine different brands of cigarette were analyzed.

Statistical analysis

For each experiment, data are expressed as mean value ± standard deviation in triplicates.

RESULTS

Standardization of Hydrosulfide (HS⁻) ion test solution

In this study, the applied standard addition method involves; the addition of known amounts of the ion to be determined to the sample solution and change in the emf of the cell was measured from standard addition modified Gran's plot method. From the measured values of emf in potentiometer, after each the addition of different volumes (V_{add}) of standard solution ($[S^{2-}]_{std}$), the Gran's function $(V_{add}+V_0)e^{-2FE/RT}$ were calculated and this function was plotted against the volume of standard solution added (i.e. V_{add}). The plot is shown in figure 1. From the intercept in V_{add} axis, V_{int} was determined in a range of - 6 for test solution. This value was then used to calculate the concentration of original sulfide ion solution. The values obtained were compared with concentration of standard solution which is shown in table 2. These two values were in good agreement with each other. This indicates the validity and reliability of standard addition method with modified Gran's plot for the determination of such a low concentration of sulfide ion as a hydrosulfide ion in aqueous solution.

Analysis of cigarette smoke solution

In this research, all together nine different brands were analyzed. Among them eight were Nepalese brands and one was international. The finding of H₂S as a hydrosulfide (HS⁻) ion in alkaline medium as mean value ± SD is shown in table 3 and graphical representation of these values is given in figure 2. Despite, H₂S content different parameters such as; weight, length, diameter and retail price per stick of each brands were also analyzed and shown in table 4

Table 1: List of cigarettes analyzed

S.N.	Sample code No.	Categories	Collected area
1	SA-1	Filter	Mahendra pool
2	SA-2	Filter	Lake side
3	SA-3	Filter	Lake side
4	SA-4	Filter	Lake side
5	SA-5	Filter	Bagar
6	SA-6	Filter	Lamachur
7	SA-7	Filter	Kahukhola
8	SA-8	Filter	Phulbari
9	SA-9	Filter	Lake side

Table 2: Comparison between the standard sulfide ion solutions

Sample Nember	Sulphide ion taken	Sulphide ion found
I	1x10 ⁻⁵ mol/Lit	0.945x10 ⁻⁵ mol/Lit
II	1x10 ⁻⁵ mol/Lit	01.04.5x10 ⁻⁵ mol/Lit
III	1x10 ⁻⁵ mol/Lit	0.855x10 ⁻⁵ mol/Lit

Mean: 0.94x10⁻⁵mol/Lit: Mean: 1x10⁻⁵ mol/Lit

Table 3: H₂S content per stick in different sample of cigarettes

S.N.	Sample code No	Hydrogen Sulfide (in mg) (Mean ± SD)
1	SA-1	0.046±0.0005
2	SA-2	0.050±0.002
3	SA-3	0.052±0.002
4	SA-4	0.047±0.002
5	SA-5	0.045±0.003
6	SA-6	0.054±0.006
7	SA-7	0.057±0.003
8	SA-8	0.055±0.002
9	SA-9	0.043±0.003

Table 4 Analysis of different parameter of cigarettes

Sample code No	Diameter (In mm)	Wt. per stick (In gm)	Length without filter (In cm)	Retail price per stick (In NRs.)
SA-1	8	0.89	6.3	10
SA-2	8	0.95	6.3	10
SA-3	8	0.71	6.3	10
SA-4	8	0.99	6.3	15
SA-5	8	0.94	6.3	8
SA-6	8	0.71	6.3	5
SA-7	8	0.76	4.8	3
SA-8	8	0.74	4.8	3
SA-9	8	70.00	6.3	20

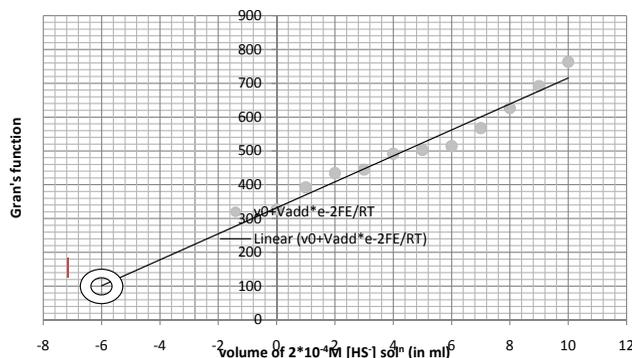


Figure 1: Standardization of hydrosulfide ion (HS⁻) by standard addition method using modified Gran's plot .

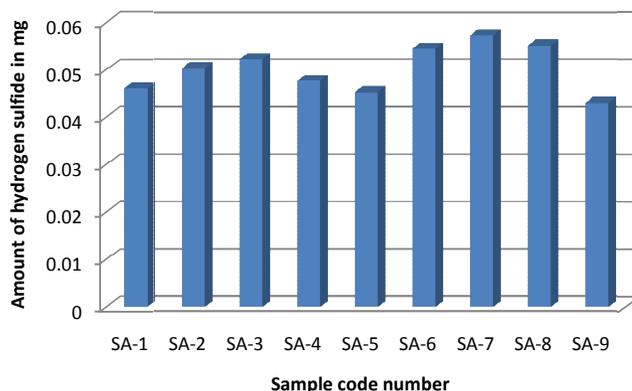


Figure 2: Graphical Representation of amount of hydrogen sulfide contain (in mg) in different sample code.

DISCUSSION

In the present study, different brands of cigarette samples were collected randomly on the basis of their sales ratios in different regions of sub metropolitan area of Pokhara. Despite, more than 3000 chemical constituents contained in cigarette smoke,¹⁵ this study focus the determination of hydrogen sulfide only. It is investigated by using standard addition with modified Grant's plot method. The applied method is superior in compared to direct potentiometry and potentiometric titration method because it has wider application for determination of hydrogen sulfide with minimum error. In addition with, it gives accurate, precise reliable and reproducible data by using cheapest chemicals and simple laboratory techniques.

Among the studied cigarette brands, there is variation in hydrogen sulfide contained per stick ranging from sample no SA-9 (0.043±0.0029SD) mg to SA-7 (0.057± 0.003SD) mg as shown in figure-2. Research finding indicated that, the sample no SA-5 has shown lower value of hydrogen sulfide contained (i.e. 0.045±0.003SD mg) in compared to SA-7 (i.e. 0.057±0.003SD mg) despite both brands is manufactured by same Nepalese company. Table 3 has shown that, the sample no SA-5 contained higher amount of hydrogen sulfide ((i.e. 0.045±0.003SD mg) in compared to SA-9 (0.043±0.0029SD mg) which is an international brand. It means the finding shows that in compared to international brands all Nepalese brands (which were taken in this research) have quite higher amount hydrogen sulfide

contained. The study also shows that standard addition method gave the better reproducible and excellent results regarding the H₂S content in the cigarette smoke¹⁶. The outcome of research tabulated in table 3 and 4, have shown that neither there is any correlation between the amount of H₂S contained nor the price, diameter, weight and length per stick of cigarette. Even the high quality and more pricey cigarette is not totally free from hydrogen sulfide contain. The result revealed that quality of cigarette is not depends on price but it depends on the quality of tobacco which is used in cigarette by cigarette manufacture company. Literature surveys have shown that hydrogen sulfide gas generated in cigarette smoke through redox process at time of combustion of tobacco in cigarette.¹⁷

CONCLUSION

The Present study concludes that the laboratory made Ag/Ag₂S ISE and Ag/AgCl reference electrodes can be used successfully to determine the hydrogen sulfide gas produced at the time of combustion of a cigarette by standard addition with modified Grant's plot method. The amount of H₂S content found in cigarette smoke of a single stick of sample code SA-5 more or less allied to the sample code no SA-9 which is one of the international brands. The standard data of H₂S contains in this brand was found to be 0.0425mg.¹⁵ This relationship has shown that the lab made Ag/Ag₂S ISE electrode would be reliable and effective to estimate amount of H₂S in cigarette smoke in any analytical laboratory.

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