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

1Komal Prasad Malla, 1Bishnu Prasad Neupane, 2Bindu Malla, 1Anil Gautam, 1Dinesh Chaudhary

1School of Health and Allied Sciences, Pokhara University, Lekhnath-12, Kaski, Nepal.
2Department of Clinical Pharmacology, Gandaki Medical College, Kaski, Nepal

ABSTRACT

Sulfurated hydrogen commonly called hydrogen sulfide (H₂S) is a clear, colorless, extremely toxic gas that has a rotten egg smell at low concentration. The human nose can detect H₂S 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 (S²⁻) ions. Sulfide ion concentration in cigarette smoke solution is found in the range of detection limit of lab made Silver- silver sulfide (Ag/Ag₂S) ion selective electrode (ISE). This project has designed to investigate the amount hydrogen sulfide as a free sulfide (S²⁻) ion in cigarette smoke solution. Silver-silver sulfide ion selective electrode (Ag/Ag₂S 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 H₂S 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,

Corresponding address: Kamal Prasad Malla, School of Health and Allied Sciences.Pokhara University, Lekhnath-12, Kaski, Nepal.
E-mail: komalmalla1971@gmail.com

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. The first cigarette factory was established in Havana in 1853 and that was set up in New Jersey of USA in 1919. 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. 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. More than 2500 constituents in tobacco leaf and more than 3,000 components in tobacco smoke have been reported by different researchers. Cigarette smoke has been intensively studied for appropriate health effects. More than forty eight different researchers have reported the existence of hydrogen sulfide in cigarette smoke. Researcher has been isolated various sulphur bearing compounds from cigarette smoke. Different authors have reported the existence of hydrogen sulfide in cigarette smokers.

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(S²⁻) ions. Due to this reason its analysis is possible in the alkaline medium. The reported threshold odor of this gas is 25ppb/0.035mg/m³. 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.\textsuperscript{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 H_{2}S per stick of different brand of
cigarettes available in local markets of Pokhara valley.

MATERIAL AND METHODS
Chemicals and Reagents
Chemicals and reagents (AgNO_{3}, Ag_{2}SO_{4}, NaOH, FeCl_{3},
KCl, Na_{2}S) 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 (Ag_{2}S) Ion selective
electrode (ISE)
The silver sulfide ion selective electrode was prepared
according to the method designed by Yadav and
Pradhananga, 1995\textsuperscript{12} with some modifications. In brief, in
100 mL of saturated solution of silver sulfate (Ag_{2}SO_{4}),
equal volumes of saturated solution of sodium sulfide
(Na_{2}S) were mixed for complete precipitation of silver
sulfide (Ag_{2}S). 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/cm\textsuperscript{2}) 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., 1980\textsuperscript{13} 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.\textsuperscript{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 H_{2}S in
the form of hydrosulfide (HS\textsuperscript{-}). 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.
2000\textsuperscript{15} 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 low.\textsuperscript{14} To check
the applicability of this method, 40 mL of 1x10^{-5}M Na_{2}S
solution were mixed in 0.1M NaOH solution taken in
a flask and 1 mL of standard 2x 10^{-4}M Na_{2}S solution in
0.1M NaOH was mixed from burette at a time till there was
an appreciable change in emf for each addition of Na_{2}S
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
H_{2}S 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^{-4}M Na_{2}S 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 (Vadd) of standard solution ([S^-]int), the Gran’s function (Vadd+Vo)e-2FE/RT were calculated and this function was plotted against the volume of standard solution added (i.e. Vadd). The plot is shown in figure 1. From the intercept in Vadd axis, V0 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    | 01.045x10^-5 mol/Lit|
| III           | 1x10^-5 mol/Lit    | 0.855x10^-5 mol/Lit|

Mean: 0.94x10^-5 mol/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                | 0.97                  | 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 reasons of sub metropolitan area of Pokhara. Despite, more than 3000 chemical constituents contained in cigarette smoke, this study focus the determination of hydrogen sulfide only. It is investigated by using standard addition with modified Gran’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 smoke. 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.

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. 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.

ACKNOWLEDGEMENT
The author expresses sincere and heartfelt gratitude to executive director of Pokhara University Research Center (PURC) for able guidance, lively discussions, honest criticisms and providing the faculty research grants. The author is thankful to School of Health and Allied Sciences, Pokhara University and Pokhara BigyanTatha Prabidhi Campus Nayabazar-9 Pokhara for providing lab facilities to conduct this research work.

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