

MEASUREMENT OF THE LEAKAGE RATES OF FOUR TYPES OF GAS GOGGLES

J. Stephenson

Safety Devices, Health and Safety Division, Ontario Hydro

Synopsis

The leakage rates of four types of gas goggles were measured with sulphur hexafluoride gas, and related to the rate which could be expected in hydrogen sulphide gas. The measurements indicate that none of the goggles had a good performance; that the model 'B' Goggle has the best performance (and was the least uncomfortable). The Model 'A' had the worst performance. The results are summarized below:

50% of the user population will be worse than:

Leakage Half-Time in H ₂ S	Time Required to Reach 50 ppm Inside the Gas Goggle in a 2000 ppm H ₂ S Environment
Model B	8.4 mins
Model C	5.7 mins
Model D	5.1 mins
Model A	2.7 mins

Acknowledgments

The author would like to express his appreciation and thanks to the following persons or groups of persons for their cooperation and/or assistance in the work program leading to the preparation of this report:

- 1) To Mr. S. Libich and Mr. H. Kaminski of the Industrial Hygiene Group for their technical advice and excellent cooperation, and for carrying out the gas chromatographic analysis of the many samples taken during the program. Also for calibrating and operating the Miran Infrared Analyzer for the last experiment in the program.
- 2) To the test subjects who endured a significant amount of discomfort over the course of the program.

- 3) To Mr. D. Agnew for his mathematical analysis of the process of diffusion of gas into and out of the goggles (Appendix 1).
- 4) Mr. R. Mitchell, the technician, who was responsible for carrying out the experimental measurements, and for the preparation of the figures showing the experimental results.
- 5) Mr. M. Stephenson, University of Guelph, for the regression analysis of each of the individual experiments.

Introduction

Since the commissioning of the Bruce Heavy Water Plant (BHPW) in the early 1970's, multi-megagrams of hydrogen sulphide (H₂S) have been stored and used at the Bruce Nuclear Power Development (BNPD) site. It is used in the heavy water extraction process. Because H₂S is a very toxic substance (Threshold Limit Value (TLV) = 10 parts/million v/v (ppm)); immediate hazard to life = 1500 ppm (1), and because it may ignite and burn to form sulphur dioxide (SO₂) (TLV = 5 ppm; immediate hazard to life = 150 ppm) (2), a large number of air purifying respirators are kept on the site to protect Ontario Hydro personnel and visitors in the event of an accidental release of H₂S/SO₂. Both gases are eye irritates at the relatively low concentration of 20 - 50 ppm (1,2).

The emergency respirator consists of a chest mounted air purifying canister which connects via a short hose to a mouth bit and nose clip breathing adapter. Gas goggles are provided with this respirator to protect the users eyes against the irritating effects of the toxic gases.

A recent attempt to define the users requirements (3) concluded that the gas goggles should provide a protection factor of 800 if the user should be exposed to gas concentrations of the order of 20,000 ppm and is not to suffer excessive

eye irritation. This observation resulted in a request to measure the protective capability of the existing, and other potentially suitable gas goggles.

The objective of the program was to measure the protective capability of four types of gas goggles, on a range of facial sizes, both male and female.

Selection of the Experimental Procedure

It was assumed that once the goggles have been donned by the user, they would be located in the most comfortable position and that they would not be subject to movements which would draw (or 'pump') the containment gas into the eye-cup space of the goggles. Consequently, the process of gaseous diffusion would be the driving force which would determine the concentration of contaminant gas into the goggles.

The process of gaseous diffusion is not significantly affected by temperature (4) (it is proportional to the square root of the absolute temperature), therefore, the temperature at which the experimental measurements are made is not very important. The rate at which gaseous diffusion occurs is also inversely proportional to the square root of the molecular weight of the gas (4).

Consequently the molecular weight of the gas selected for the experimental measurement of leakage rates into the gas goggles relative to the molecular weight of H_2S , must be taken into account before the final conclusions are reached.

Two additional assumptions were made to limit the scope of the experimental measurements. These were:

- 1) That each member of the population of a given type of goggle is identical to every member. This assumption is based on the fact that the goggles in question are all mass produced using precision molding techniques. The inference is that it is not necessary to evaluate the performance of more than one goggle of each kind.
- 2) That the degree of 'fit' obtained by a goggle user would change each time a goggle is used, and that the distribution of the range of fits will be log normal (i.e. it will be similar to the distribution of fits obtained when a person dons a full facepiece respirator (5)). This assumption implies:
 - a) That it is not necessary to measure the

range of 'fits' obtained by each person.

- b) That range of 'fits' obtained with a test panel will probably also have a log normal distribution.

Two possible experimental procedures were considered.

The first was to expose the test subject(s) in an environmental chamber containing a suitable (harmless?) gas contaminant. The gas concentration inside the goggles must then be measured, at intervals, while the test subject performed an appropriate exercise program. At the same time the sampling process must not prejudice the rate of leakage into the goggle, nor must the samples be spoiled by exposure to a high gas concentration.

The second approach was to pump a small concentration of suitable gas into each eye cup of the gas goggles, then to measure the rate of decay of the gas concentration. This method has several advantages:

- It needs small quantities of the gaseous contaminant.
- The test subject exercises in a normal environment.
- There is little chance of contaminating the samples.

Mathematically the gas concentration inside the goggles is given by $C = C_0 e^{-rt}$ if it is assumed that the leakage rate is constant. This process is the inverse of the real process in which the gas leaks into the goggles. ($C = C_0 (1 - e^{-rt})$). In both cases C_0 is the environmental contamination; C is the concentration inside the goggles; r is the leakage rate constant and t is the time of exposure (minutes).

There are potential disadvantages of problems with the second procedure:

- The eye cup is presented when the contaminant gas is introduced, but the problem was minimized by injecting only a few microlitres into the eye-cup space.
- The procedure is not sensitive to small changes in gas concentration, but small changes in concentration would imply an excellent degree of gas tightness.
- The sampling process may cause a pumping action on the gas goggles which would give an artificially high rate of leakage.

The test gas was selected on the basis that it would be inert and essentially harmless to the test subject. After considering various possibilities, sulphur hexafluoride (SF_6) was selected for the

experiment:

- It is easily measured at ppm concentration using gas chromatography techniques. It can also be measured at hundreds of ppm using infrared techniques.
- It is considered to be inert and essentially harmless to test subjects.
- It is not likely to be absorbed to any significant extent by body fluids, or the components for the gas goggles.
- It was readily available and (in the quantities required) low in cost.

Other gases considered but not selected included:

Carbon-14 dioxide and freon.

We were advised that SF₆ could be measured by means of Hewlett Packard 5880A gas chromatographic analyzer having a 6 m long, 0.25 mm internal diameter, DB5 capillary chromatographic column. Hydrogen was used as a carrier gas, with a column velocity of 25 cm/sec., at room temperature (21 °C to 25 °C).

A primary dilution of SF₆ was prepared by injecting 640 microlitres (μl) of SF₆ into a 32 ml gas tight glass vial (containing air) in order to give 20,000 ppm of SF₆ in air. Chromatographic Calibration Standards were prepared by injecting 5, 10, 15 and 20 μl of primary dilution into each of 4, 32 ml gas tight glass vials. These standards were used for constructing calibration curves for the GC each time it was used. The precision of the sampling technique using gas tight micro syringes was tested by preparing a dilution of approximately 15 ppm of SF₆ in air. 10 individual samples were taken. The peak areas were measured by an integrating recorder (Table 1).

In the final experiment, a Miran Infrared Analyzer, Type LA, was used to monitor SF₆ concentrations on a continuous basis over a period of 15 to 20 minutes. This instrument was calibrated for SF₆ by putting it into "closed loop circulation." Specific volumes of SF₆ were injected into the known volume of air in the closed loop. A calibration curve was then constructed by relating the calculated SF₆ concentration (in the air in the closed loop) to the amplitude of the meter readout).

Selection of Test Subjects

Test subjects were selected on the basis of their availability and willingness to participate in the experimental program. Seven males and three females volunteered. Key dimensions of their

TABLE 1

Assessment of the precision of the sampling technique using gas tight microsyringes and gas chromatographic analysis:

Sample Number	Peak Area x 10 ²
1	1425
2	1355
3	1402
4	1434
5	1429
6	1432
7	1383
8	1393
9	1386
10	1404
$\bar{x}$	1404
S_x	2574

$\bar{x}$ = population means

S_x = sample standard deviation

$$\mu = \bar{x} \pm \frac{S_x}{\sqrt{n}} \cdot t$$

where

n = number of elements in the sample

t = value for the number of degrees of freedom from 't' tables for 95% confidence interval

2574

$$\mu = 140430 \pm \frac{2574}{\sqrt{10}} \cdot 2.28$$

$$= 140430 \pm 1940$$

i.e. the mean of the 10 analysis is 140430 with 95% certainty that it is correct to $\pm 1.38\%$.

The sample standard deviation S(x) is 2574.

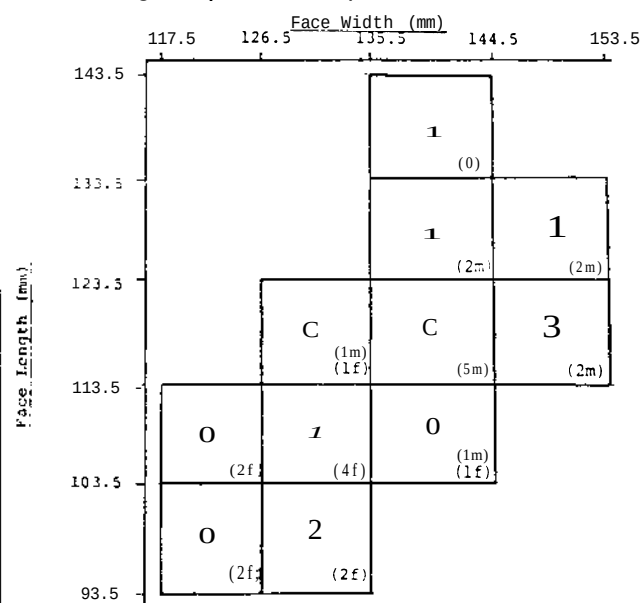
$\therefore$ the 95% confidence limits for each sample is

$$\frac{2574 \times 2}{140430} \times 100 = 3.67\%$$

facial sizes were measured and recorded. Figure 1 shows the distribution of facial sizes relative to the Los Alamos 25 member anthropomorphic test panel for evaluating the performance of respirators with respect to a population of American people (7). Figure 1 shows that the larger sizes of men are represented in our test subjects, as are the larger sizes of women. The smaller sizes of men and women are absent.

Figure 1

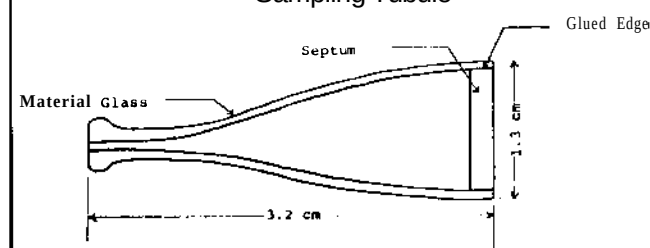
Facial Sizes of Test Subjects Related to the Facial Sizes of the Los Alamos 25 Member Panel for Testing Respirator Facepieces



Figures in parenthesis show the distribution of the American 25 Member Panel

Experimental Procedure

Using a gas-tight microsyringe, 5 μ l of SF₆, or more depending upon the size of the eye-cup) from the primary dilution vial, were injected into the right and left eye-cups of each of the goggles, at times 0 and =1 minute respectively with the test subject sitting on a stool in the gas chromatography laboratory. Using clean gas tight microsyringes, after 'pumping the syringe 3 times to allow the internal surfaces of the syringe to equilibrate with the gas concentration in the eye cup, 5 μ l samples were taken from each eye cup in turn, at times +2 mins and +3 minutes. This sampling procedure was repeated at +7 and +8 minutes. The test subject was then required to walk to the respirator test laboratory situated in another part of the building - a distance of approximately 75 paces. He was then asked to sit on a stool until samples had been taken, as before, at times +12 and +13 minutes. The test subject then walked on a treadmill at 4 kilometers per hour; set at an incline of approximately 2.5°, for two, approximately 5 minute periods. Samples were taken from the goggles at +17 and +18 minutes, and at +22 and 23 mins. The test subject then retraced his steps to the G.C. laboratory for final samples at +27, +28 mins., after which the goggles were removed.

Figure 2
Sampling Tubule

Modifications to the Goggles

In order to facilitate the injection of SF₆ into the eye space of each goggle, and the subsequent sampling program, each goggle was modified by inserting a small glass tubule through the wall of the goggle. The other end of the tubule was closed with a silicone sampling septum which was cemented in place. The main reasons for this modification were:

- 1) To provide safe access to the eye space for the hypodermic needle. (The glass tubule

Figure 3
Model AFigure 4
Model BFigure 5
Model CFigure 6
Model D

acted as a guide and helped the technician to locate the tip of the needle inside the goggle).

- 2) To enable repeated samples to be taken through the wall of the goggle without significantly affecting the integrity (or the gas tightness) of the elastomer of the goggles.

A cross section of the sampling tubule is shown in Figure 2. Photographs of the four types of goggles with tubules in place are shown in Figures 3 through 6.

Procedure for Donning the Goggles

Each test subject was shown how to don and adjust the goggles so as to obtain a good fit. He/she was then asked to don the goggles unaided and to adjust them to the best possible fit, as if he or she was to wear them in a real H₂S release. Once the goggles were adjusted, and as comfortable as possible, they were not further adjusted for the duration of the experiment.

Comments on the Effect of Sampling from the Goggles

Five μl of gas containing 20,000 ppm of SF₆ were injected into each eye cup of the goggles. Each eye cup was separated from the other by the nose-bridge piece in 3 of the goggle styles. The 4th style had a single visor extending across both eye, i.e. there was no central seal across the bridge of the nose. Consequently, there was only one cavity in this style of goggle. (This fact must be kept in mind when the results of the experiments are discussed).

If the SF₆ concentration in the goggle, after injecting 5 μl of the primary dilution, is measured, the volume of the eye cup space can be calculated. In the case of the Model B Goggle, the eye space was calculated to be approximately 20 ml. Five μl is approximately 0.025% of the eye cup volume. The pressure rise associated with this added volume is considered to be negligibly small. The same conclusion can be reached - that removing 0.025% of the eye cup volume would have a negligible effect on the pressure inside the goggle. Also, the introduction of 5 μl of air to replace the sample volume would have a negligible effect on the SF₆ concentration inside the eye cup space - reducing the SF₆ concentration

by approximately 2 parts in 10⁷.

The action of inserting the hypodermic needle through the sampling septum into each eye space; 'pumping' the syringe and the subsequent withdrawal of the needle from the septum, caused small movements of the goggle on the face. Although the goggle was steadied by the test subject (by carefully grasping it so as to hold it still) during the sample process, it is not possible to rule out the possibility that the process of sampling exacerbated the leak rate.

Experiment to Test for Absorption of SF₆ Into Goggle Components or Body Tissues

It was hypothesized that SF₆ would not be absorbed to any significant extent in the elastomeric components of the goggles, or into the body tissues or fluids. Consequently, if it could be arranged that the goggles did not leak, there should be no change in the SF₆ concentration in the eye cup.

Model 'A' goggle was selected for the first test of the hypothesis. Six test subjects were asked to don goggles which had a liberal coating of petroleum jelly (vaseline) on the surface which sealed to the skin. The outer edge of the goggle/skin seal was also carefully inspected, and additional vaseline applied when necessary in order to try to ensure that the goggles would not leak. In addition, the test subjects were asked to sit on a stool in the GC laboratory and to minimize both body and facial movements, over the duration of the experiment in order to try to ensure that the goggles would not leak.

The results of this experiment are given in Tables III (a) and (b).

Table III (a) indicates that subjects 3 and 4 achieved near zero leakage from one eye cup and subjects 2 and 5 had small leakages (6.7% and 5.5% respectively) from one eye cup each.

Table III (b) gives the results of a linear regression analysis on each set of data in Table III (a).

Linear regression analysis was used to draw the best straight line through each set of experimental data, from which the slope of the line could be determined and the leakage half-time (T_{1/2}) calculated.

TABLE III (a)
Variations in SF₆ Concentrations in Eye Cups of Model 'A' Goggles
Sealed to the Face with Petroleum Jelly

		Sampling Time (Minutes after Start) (Concentration ppm)					
Test Subject Number	Eye	2/3	7/8	12/13	17/18	22/23	27/28
3	R	16.2±0.6	16.8±0.6	17.2±0.6	16.7±0.6	15.4±0.6	16.5±0.6
	L	15.7±0.6	14.6±0.5	14.0±0.5	14.7±0.5	14.6±0.5	14.9±0.5
5	R	14.8±0.5	8.4±0.3	7.9±0.3	3.8±0.1	3.2±0.1	1.7±0.1
	L	16.2±0.6	16.0±0.6	15.5±0.6	15.4±0.6	15.4±0.6	15.3±0.6
4	R	9.9±0.4	8.2	7.6	6.8	6.1	5.5±0.2
	L	10.9±0.4	10.9	10.9	10.8	10.8	10.8±0.4
6	R	14.2±0.5	14.2	14.0	13.5	12.7	11.9±0.4
	L	16.0±0.6	16.0	15.8	14.8	13.8	13.2±0.5
2	R	9.9±0.4	9.3	7.8	7.1	6.7	6.5±0.2
	L	12.0±0.4	12.0	11.8	11.2	11.7	11.2±0.4
10	R	11.9±0.4	11.9	11.5	11.7	11.2	11.4±0.4
	L	13.3±0.5	12.7	12.3	11.3	10.9	10.1±0.4

The procedure was based on the logarithmic form of the equation $C = C_0 e^{-rt}$.

viz. $\log C = \log C_0 - 0.4343 rt$

which is linear in the form $y = k + mx$

The logarithm of the measured gas concentration in the eye cup was plotted against t , the time the sample was taken. C_0 is the intersection of the line on the ordinate and the slope of the line, $m = 0.4343r$.

The leakage half time ($T_{1/2}$) occurs when $C = \frac{1}{2} C_0$

$$\text{or } \frac{C}{C_0} = e^{r(T_{1/2})} = 2$$

$$\therefore \log 2 = 0.4343r(T_{1/2})$$

$$\text{or } T_{1/2} = \frac{0.301}{m}$$

TABLE m (b)
Regression Analysis of Data in Table III(a)

Test Subject Number	Eye	Slope	Correlation Coefficient	Calculated T 1/2 (mins)	Confidence Level
3	R	-0.0012	-0.305		
	L	-0.0011	-0.279		
5	R	-0.0826	-0.983		
	L	-0.0023	-0.92	301	> 99%
4	R	-0.022	-0.993		
	L	-0.00047	-0.878	1474	> 95%
6	R	-0.0072	-0.936		
	L	-0.0084	-0.951		
2	R	-0.0182	-0.972		
	L	-0.027	-0.798	256	> 90%
10	R	-0.0022	-0.830	315	> 95%
	L	-0.011	-0.992		

Test subjects 4, left eye had a leakage half time of 1474 minutes while test subjects 5 (left eye), 2 (left eye) and 10 (right eye) had leakage half times greater than 250 minutes. As will be seen from data presented later in this report, these leakage half times are in order of magnitude or more longer than the leakage half times measured on test subjects wearing the gas goggles in a normal manner. It is concluded that if SF₆ is absorbed into eye tissues or fluids, skin, or goggle components, the quantity absorbed can be regarded as being negligibly small for the purpose of these experiments.

A similar experiment was carried out using the Model B goggle, except that only one test subject was used. Two measurements were made because of a failure to achieve a near zero leakage, even when the goggles were apparently well sealed with vaseline. The main problem with the petroleum jelly was that it softened and ran down the test subject's face when it reached skin temperature; A final (i.e. 3rd) experiment was carried out using 'high vacuum' grease, which has a higher melting point. The data obtained in three experiments is shown in Table IV(a).

TABLE IV(a)
Change in SF₆ Concentration in Model B Goggles Sealed to the Skin with
'Petroleum Jelly' and High Vacuum' Greases

Experiment Number	Eye	Sampling Time (Minutes after Start) (Concentration ppm)					
		27/2	2/3	7/8	12/13	17/18	22/23
1	R	4.6±0.2	4.4	4.0	3.6	3.1	3.1±0.1
	L	4.8±0.2	4.0	2.0	2.0	1.2	1.1±0.05
2	R	4.2±0.2	4.1	3.8	3.4	3.4	3.3±0.1
	L	5.4±0.2	5.0	4.8	4.6	4.4	4.2±0.2
3	R	16.8±0.6	17.6±0.7	13.0±0.5	11.8±0.4	13.0±0.5	13.2±0.5
	L	14.0±0.5	13.4±0.5	13.2±0.5	13.6±0.5	13.1±0.5	13.0±0.5

Table IV(b) gives the result of linear regression analysis on each set of data in Table IV(a).

The half times given in Table IV(b) illustrate the difficulty of obtaining a good seal with the Model B Goggle. Alternatively they indicate that the SF₆ is absorbed into tissues, eye fluids or goggle components. However, the long T 1/2

obtained in the experiment 3 (left eye) - 301 mins. suggests that the overall problem is leakage, rather than absorption of SF₆. It is concluded that the absorption of SF₆ into skin, eye fluids, eye tissues, or goggle components is acceptably small for the purpose of measuring gas leakage from the goggles.

TABLE IV(b)
Linear Regression Analysis of Data in Table IV(a)

Experiment Number	Eye	Slope	Correlation Coefficient	Calculated T 1/2 (mins)	Confidence Level
1	R	-0.0177	-0.986	39	> 99%
	L	-0.063	-0.97	11	> 99%
2	R	-0.011	-0.95	63	> 99%
	L	-0.0085	-0.999	81.5	> 99%
3	R	-0.0126	-0.736	55	> 90%
	L	-0.0023	-0.794	301	> 90%

Assessment of the Protection Afforded by the Goggles

Model 'A' Goggles

Ten subjects (7 male, 3 female) were used to test the performance of the Model 'A' Goggle using the protocol outlined previously. The data obtained is presented in Table V. Figure 7 shows the data for male right eyes.

During the course of the above measurements all of the subjects complained of 'fogging' of the goggle lens in times as short as 2 minutes and as long as 7 minutes. In all cases the fogging only partially obscured vision.

Six of the test subjects complained that the goggle was painful to wear in one or more respects. One person complained of a headache

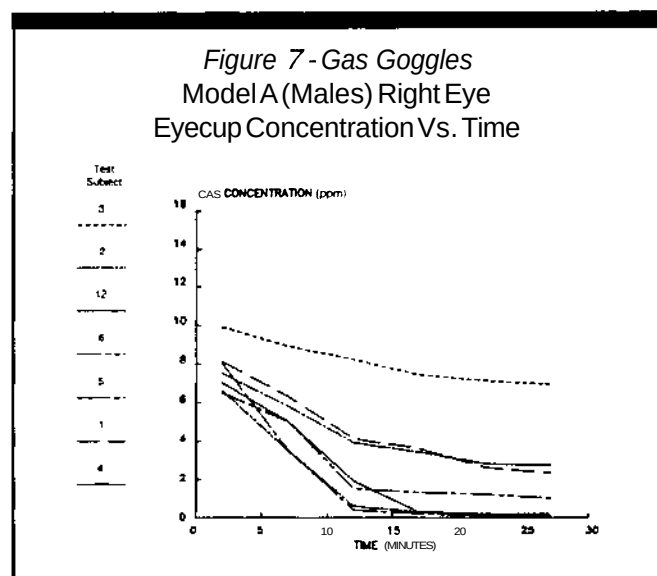


TABLE V
Experimental Data for Test Subjects Wearing Model 'A' Goggles

Test Subject Number	Eye	Sampling Time (Minutes after Start) (Concentration ppm)					
		2/3	7/8	12/13	17/18	22/23	27/28
1	R/L	8.1/7.8	6.3/6.0	4.1/4.1	3.6/3.2	2.6/2.6	2.3/2.1
12	R/L	7.5/8.0	5.8/7.1	3.9/5.7	3.4/5.0	2.8/4.2	2.7/3.8
2	R/L	6.6/7.4	3.5/4.7	0.6/0.8	0.3/0.7	0.2/0.3	0.2/0.2
4	R/L	7.0/8.0	5.0/5.7	1.9/3.5	0.3/0.9	<0.1/0.3	<0.1/0.2
5	R/L	8.0/10.2	3.5/7.1	0.4/5.8	0.2/5.1	<0.1/4.1	<0.1/3.2
6	R/L	6.5/8.4	5.0/7.3	1.5/2.9	1.3/1.9	1.2/1.0	1.0/0.8
8	R/L	7.2/7.9	3.1/1.6	0.7/0.3	0.3/0.3	0.1/0.2	0.1/0.2
9	R/L	8.0/9.8	3.8/3.4	0.6/0.6	0.3/0.6	0.1/0.4	0.1/0.2
3	R/L	9.8/8.9	8.9/5.6	8.2/3.3	7.4/2.6	7.1/1.7	6.9/1.2
11	R/L	8.6/6.8	5.2/2.1	2.0/0.5	1.4/0.5	0.7/0.3	0.4/0.2

and two of pain over the ears related to the retaining strap. Most of the complaints related to pressure of the goggle on some part of the face. Not one of the test subjects obtained a good fit with a 30% leakage over the 28 minute test period. The worst performance (Test Subject #8, left eye) was a 79.7% leak in the first 5 minutes. Analysis of the data is discussed in the next section of this paper.

Model 'B' Goggles

Ten subjects (7 male, 3 female) volunteered to

wear the Model 'B' goggle. The test was carried out in the same manner as described above. The data obtained is presented in Table VI, and Figure 8 shows the data for male right eyes.

The Model 'B' goggle was considered to be much more comfortable than the Model 'A' goggle - only 4 of the subjects complaining of pain or discomfort after 15 minutes of wear. There were fewer complaints of lens fogging, but when complaints were made, they were made in the first few minutes of wear.

The data shown in Table VI and in Figure 8

TABLE VI
Experimental Data for Test Subjects Wearing Model 'B' Goggles

Sampling Time (Minutes after Start) (Concentration ppm)

Test Subject	Eye	2/3	7/8	12/13	17/18	22/23	27/28
1	R/L	4.0/4.8	3.4/3.8	3.4/3.4	3.1/1.9	2.4/1.1	2.1/1.0
2	R/L	3.4/3.4	3.4/3.2	3.1/2.1	3.0/2.0	2.7/1.4	2.3/0.6
3	R/L	4.4/5.0	4.0/4.1	3.6/3.1	3.6/2.7	3.3/2.4	3.2/2.0
4	R/L	3.3/3.6	2.7/2.8	2.5/1.7	2.3/1.7	2.0/1.1	1.9/1.0
5	R/L	4.5/5.0	4.3/4.3	3.9/2.4	3.6/2.0	3.2/1.5	2.8/1.0
6	R/L	4.8/5.2	3.0/3.9	1.7/2.6	1.4/2.2	0.8/1.5	0.5/1.0
8	R/L	3.6/4.3	3.1/3.8	2.6/3.1	2.0/2.1	1.7/1.7	1.4/1.3
9	R/L	2.5/3.0	1.9/2.6	1.1/2.0	1.0/1.6	0.8/2.1	1.0/1.7
11	R/L	4.3/4.3	4.0/3.3	3.4/2.3	3.1/2.1	2.6/1.6	2.1/1.6
12	R/L	4.0/4.2	3.5/3.1	2.7/2.0	2.2/1.6	1.6/0.6	1.4/0.6

indicates that the Model 'B' goggle has less leakage than the Model 'A' goggle, but again not one of the test subjects obtained a good fit, even for one eye. The lowest leakage over the period of the experiment was approximately 27%; the highest was 89%. Analysis of the data is discussed in the next section of this paper.

Model 'C' Goggles

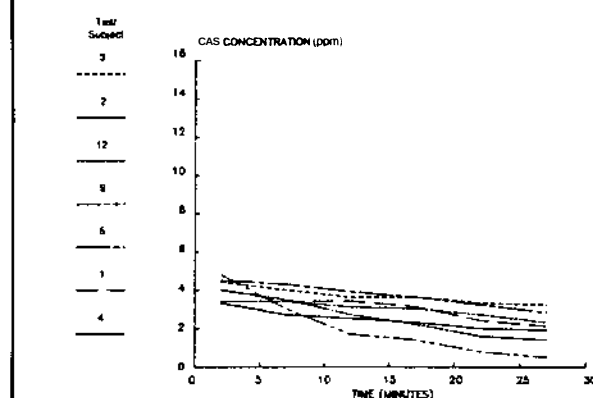
Eight subjects (6 male, 2 female) were used in this evaluation. The data obtained is shown in Table VII. Fig. 9 shows the data for male right eyes.

These goggles were considered to be the most uncomfortable by all of the test subjects. Several subjects complained of pressure points.

Again, most subjects complained that the lens of the goggle were getting foggy within a few minutes of the start.

Several measurements of SF_6 concentration in this series appear to be higher or lower than expected. The most probable explanation for this phenomenon is that the needle of the hypodermic syringe had become partially blocked, leading to imperfect sampling. Other possible explanations include poor mixing of the SF_6 in the small eye cup (which this goggle has) or to leakage across the bridge of the nose from one eye cup to the other. The smallest leakage is difficult to identify because of the uncertainty in the initial concentrations for some of the test subjects. However, Test Subject #1, left eye appears to have lost 45% of the SF_6 over the

Figure 8 - Gas Goggles
Model B (Males) Right Eye
Eyecup Concentration Vs. Time



duration of the experiment, while Test Subject #12, right eye has a 95% leakage. Analysis of the data is discussed in the next section of this paper.

Model 'D' Goggle

Nine (9) subjects (6 male, 3 female) volunteered for this experiment. The data obtained is presented in Table VIII. Figure 10 shows the data for male right eyes.

This goggle may be considered to have only one eye space - though with some test subjects the nose will tend to separate the eye space into two compartments.

TABLE VII
Experimental Data for Test Subjects Wearing Model 'C' Gas Goggles

Test Subject	Eye	Sampling Time (Minutes after Start) (Concentration ppm)					
		2/3	7/8	12/13	17/18	22/23	27/28
1	R/L	13.6/6.7	12.1/6.4	5.2/5.8	3.9/5.0	2.5/4.7	2.1/3.7
2	R/L	7.2/6.0	8.1/4.6	5.6/4.3	4.0/4.0	3.6/3.3	2.9/2.0
4	R/L	6.9/5.8	5.2/6.1	-11.9(?)	4.4/8.3	3.4/6.4	3.2/6.0
5	R/L	20(?) / 7.4	10.4/12.0	9.8/9.3	6.3/8.4	4.2/8.6	4.2/7.6
6	R/L	15.5/11.7	7.8/8.0	5.0/6.9	3.0/7.2	1.5/5.5	1.2/2.2
8	R/L	7.9/8.2	5.3/5.4	3.9/3.5	2.6/2.9	1.8/2.2	1.2/2.5
11	R/L	17.0/12.3	10.9/8.2	6.7/8.1	3.9/6.1	2.8/6.4	2.5/4.0
12	R/L	24.5/14.4	12.2/13.0	3.0/14.2	4.5/8.2	2.0/11.6	1.2/8.8

Figure 9 - Gas Goggles
Model C (Males) Right Eye
Eyecup Concentration Vs. Time

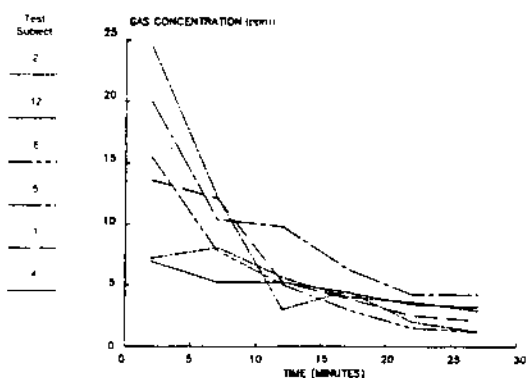


Figure 10 - Gas Goggles
Model D (Males) Right Eye
Eyecup Concentration Vs. Time

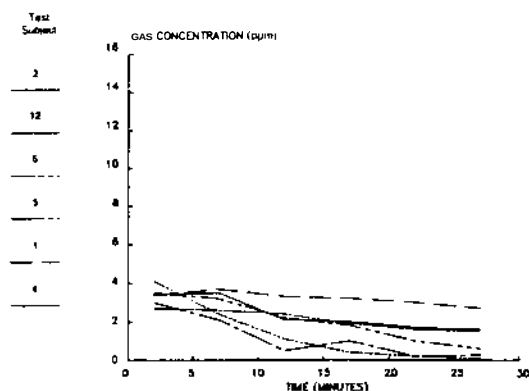
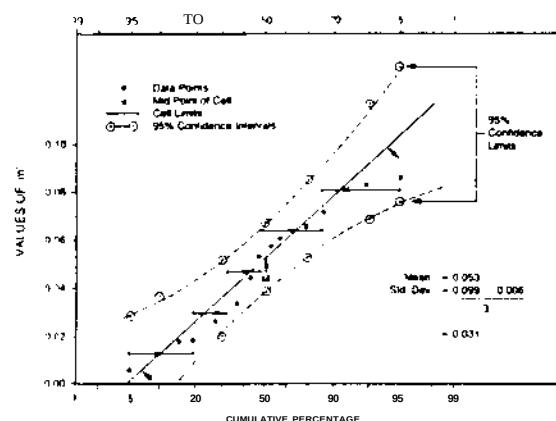


Figure 11
Model A



In 8 of the 10 measurements the left eye has a higher concentration than the right eye. The right and left eye spaces would be expected to have similar concentrations if diffusion from one eye space to the other was occurring with reasonable rapidity. This is not generally seen, within the 95% limits of confidence established for the precision of the analytical method, as established at the beginning of the experimental program.

This goggle has a semi-rigid frame; it is necessary to distort the frame away from its natural position in order to achieve a reasonable degree of fit on some test subjects. This, in turn, requires that the headband be tight, and results in some discomfort due to pressure points over the eyes or on the cheek bones.

TABLE VIII
Experimental Data for Test Subjects Wearing the Model 'D' Goggles

Test Subject	Eye	Sampling Time (Minutes after Start) (Concentration ppm)					
		2/3	7/8	12/13	17/18	22/23	27/28
1	R/L	3.4/4.6	3.7/4.2	3.3/3.8	3.2/3.4	3.0/3.3	3.7/3.0
2	R/L	4.1/3.6	2.4/1.3	1.1/0.3	0.4/<0.1	0.2/0.1	0.1/<0.1
4	R/L	3.4/4.4	3.5/3.9	2.1/2.7	2.0/2.2	1.7/2.0	1.6/1.6
5	R/L	3.2/2.0	0.1/0.2	<0.1/0.2	<0.1/<0.1		
6	R/L	3.5/4.6	3.2/3.2	2.2/1.4	1.8/1.6	1.0/0.4	0.6/0.4
8	R/L	3.9/4.5	3.8/3.9	3.4/3.6	3.2/3.0	2.8/2.8	2.8/2.5
9	R/L	3.8/4.7	3.0/1.8	1.7/1.3	1.3/1.3	1.0/0.7	0.6/0.3
11	R/L	2.7/3.7	0.2/0.3	0.1/0.2	0.1/0.1	0.1/0.1	0.1/0.1
12	R/L	2.7/3.3	2.6/3.8	2.4/3.0	1.9/2.8	1.6/2.2	1.5/1.6
5 (repeat)	R/L	3.0/5.0	2.1/3.8	0.5/2.1	1.0/1.5	0.2/1.0	0.3/0.6

Some of the test subjects commented that they did not think they had achieved a very adequate seal, or that they felt that the seal had broken if they laughed, or wrinkled the face to relieve discomfort.

A review of the data in Table VIII suggests that none of the subjects obtained a good fit with this goggle. The lowest leakage (test subject #8, right eye) over the 27 minute experiment was approximately 28%. The highest leakage (test subject #2, right eye) is approximately 98%.

Interpretation of Data

A regression analysis was performed on the data for each experiment in order to obtain the best estimate of the slope of the curve (m) and the corresponding value of the correlation coefficient (R^2). (Tables 9, 10, 11 and 12).

Because of the relatively small number of test subjects for each type of goggle, the data for the right and left eyes were combined and treated as one 'distribution'.

Also, those sets of data where the gas concentration in an eye cup increased by more than one standard deviation of the measured concentration (based on the expected precision of the analytical procedure) were discarded (this condition infers that the sampling process was defective).

TABLE DC
Regression Analysis on Model 'A' Goggles
Left Eye Right Eye

Test Subject	Left Eye		Right Eye	
	m	R^2	m	R^2
1	-0.023	.988	-0.023	0.976
2	-0.066	.941	-0.066	0.891
3	-0.034	.991	-0.006	0.959
4	-0.071	.96	-0.086	0.941
5	-0.019	.981	-0.083	0.902
6	-0.045	.969	-0.034	0.839
8	-0.061	.789	-0.081	0.957
9	-0.064	.898	-0.083	0.943
11	-0.058	.891	-0.054	0.990
12	-0.013	.991	-0.018	0.937

The values of m, obtained from the regression analysis, for each model, were then plotted on log-probability paper using the procedure given in reference 8. It was observed that the data for Model 'A' goggles gave a distinctly curved line. This implied that the data did not have a log-normal distribution.

Consequently, the data was re-plotted on normal probability paper. A straight line was drawn through the data points although the 'fit' was not considered to be good.

The fact that the data does not appear to have a

TABLE X
Regression Analysis on Model 'B' Goggles
Left Eye Right Eye

Test Subject	m	R ²	m	R ²
1	-0.03	0.95	-0.011	0.929
2	-0.028	0.88	-0.007	0.909
3	-0.016	0.982	-0.006	0.962
4	-0.023	0.954	-0.009	0.97
5	-0.008	0.979	-0.038	0.991
8	-0.022	0.982	-0.017	0.995
9	-0.018	0.779	-0.009	0.668
11	-0.018	0.94	-0.012	0.976
12	-0.037	0.947	-0.019	0.989

TABLE XI
Regression Analysis on Model 'C' Goggles
Left Eye Right Eye

Test Subject	m	R ²	m	R ²
1	-0.01	0.951	-0.036	0.957
2	-0.016	0.885	-0.018	0.921
5	-	-	-0.027	0.937
6	-0.023	0.8	-0.045	0.988
8	-0.022	0.881	-0.032	0.999
11	-0.016	0.897	-0.035	0.971
12	-0.008	0.543	-0.05	0.897

TABLE XII
Regression Analysis on Model 'D' Goggles
Left Eye Right Eye

Test Subject	m	R ²	m	R ²
1	-0.007	0.984	-	-
2	-0.066	0.858	-0.067	0.994
4	-0.018	0.974	-0.015	0.884
5	-0.037	0.993	-0.044	0.785
6	-0.045	0.916	-0.031	0.949
8	-0.01	0.989	-0.007	0.957
9	-0.041	0.925	-0.032	0.986
11	-0.055	0.704	-0.046	0.566
12	-0.013	0.836	-0.011	0.951

log-normal distribution may imply that the fit of the goggles on the test subjects was not log-normal (i.e. is contrary to the initial basic assumption). However, there is a possibility that the data obtained for the right and left eyes respectively, may belong to two different distributions - in which case they should not have been combined.

The conclusion that the rate constants for the Model 'A' goggles have a normal distribution should therefore be accorded a degree of caution. (Further experimental measurements would be needed to resolve this question).

The data for the Model 'A' goggle is summarized in Table 13 and shown in Figure 11.

The values of m obtained for the model B, C, and D goggles were reasonably consistent with the hypothesis that the fit of the goggles would have a log-normal distribution. The data is summarized in Table 14 and shown in Figures 12, 13 and 14.

Comparison Between Inleakage and Outleakage Rates of SF₆

Because there was a significant possibility that the sampling procedure increased the leak rate of the goggles, it was decided to try to compare the leak rate measured by both inleakage and outleakage techniques. The procedure adopted was to measure the outleakage of a goggle worn by one of the test subjects. Then, without moving or adjusting the fit of the goggles, a hood was placed over the test subjects's head and sealed around his neck by means of a drawstring. The test subject was supplied with breathing air by means of a mouthpiece which was connected to a demand type compressed air supplied respirator, which penetrated through the wall of the hood. A nose clip sealed the subject's nose. The test subject's exhaled air was discharged into the hood. At the same time 40 l per minute flow of air containing 1000 scfm of SF₆ was pumped into the hood in order to maintain an approximately constant concentration of SF₆ inside the hood. The concentration of SF₆ inside the hood was monitored and measured on a continuous basis by a Miran Infrared Analyzer which drew 10 to 20 l/min flow of SF₆ contaminated air from the hood, then passed it through the analyzer and back into the hood.

The test subject was then asked to walk for a 15 minute period on a treadmill running at 4 kilometer/h on a 2.5° incline. At the end of the 15

minute period, the hood was removed, and both eye cups were sampled in the usual manner.

The measured SF_6 concentrations were:

Left Eye: 150 ppm Right Eye: 200 ppm

The regression analysis for the data obtained in the outleakage part of the experiment is shown in Figure 15.

Right and left eye values of m were -0.036 and -0.037 respectively.

Substituting these values in turn into the equation

$$C = C_0(1 - e^{-rt})$$

where $C_0 = 600$ ppm

$t = 15$ mins.

gives values of C equal to

1) Right eye 250 ppm 2) Left eye 257 ppm

These values may be compared with the measured values of 200 ppm and 150 ppm for the right and left eyes respectively. The measured values are therefore a little lower than the predicted values. There may be several reasons for this - the most likely being that the pumping action imposed on the goggles during the sampling process slightly increases the apparent leakage rate. Other possible reasons include:

- 1) that the goggles may have 'settled into' the face to give a better seal and hence of lower leakage rate.
- 2) the goggles may have been moved slightly when the hood was donned and the degree of fit slightly improved.

Whatever the actual reasons for the 'slightly better than predicted' performance, the important conclusion is that the experimental method of measuring the leakage rate constant is not wildly out.

Correction for the Molecular Weight of Contaminant Gas

Graham's Law of Diffusion may be written in the form

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}}$$

where M_2 = molecular weight of $\text{SF}_6 = 146$

M_1 = molecular weight of $\text{H}_2\text{S} = 34$

and D_1 and D_2 are the rates of diffusion for H_2S and SF_6 respectively.

$$D_1 = D_2 \sqrt{\frac{146}{34}} = 2.07 D_2$$

i.e. the rate constant for H_2S will be approximately 2.1 x the rate constant obtained for SF_6 .

Figure 12
Model B

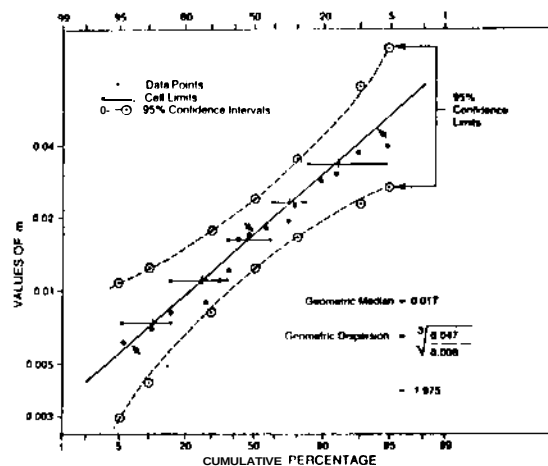


Figure 13
Model C

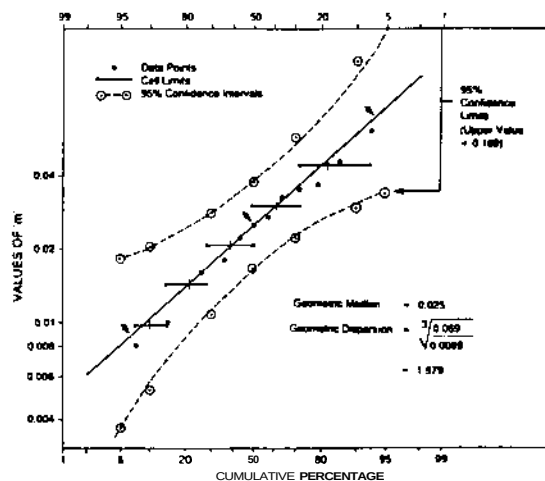


Figure 14
Model D

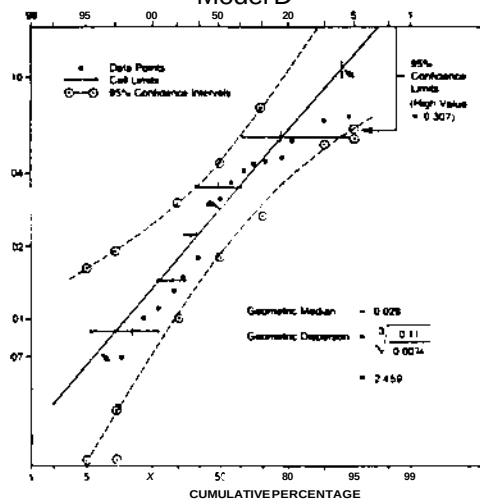


TABLE XIII
Summary of Data for Model 'A' Goggles

Model	Mean Value of M	Std. Dev.	Mean Leakage Rate Constant	Mean Leakage Half-Time
Model 'A' Goggles	-0.053	0.031	-0.122	5.7 mins

TABLE XIV

Summary of the Data for Model B,C, and D Goggles

Model	Median Value of m	Geometric Dispersion	Median Leakage Rate Constant	Median Leakage Half-Time
B	-0.017	1.975	-0.039	17.7 min
C	-0.025	1.979	-0.057	12.0 min
D	-0.028	2.459	-0.064	10.8 min

Table IX shows the median leakage half times for H₂S leaking into each of the four goggles.

TABLE 15
Leakage Half Times for
H₂S Into the Gas Goggles

<u>Goggle</u>	<u>Median Leakage Half Time</u>
Model B	8.4 mins.
Model C	5.7 mins.
Model D	5.14 mins.
Model A	2.7 mins.

General Discussion

The question which has to be answered is "do any of the goggles offer an adequate level of protection?" This may be answered by considering the time required for the concentration inside the goggle to rise to the point where eye irritation will be a potential problem.

Consider an incident in which we have 2000 ppm of H₂S in the environment. How long will it take for 50% of the exposed population to have more than 50 ppm of H₂S in the eye cup of the Model B goggles?

We can calculate a value for m using the median leakage half-time of 8.4 mins (for H₂S) and the relation:

$$T_{1/2} = \frac{-0.301}{m}$$

$$m = \frac{301}{8.4} = 0.0358$$

$$\begin{aligned} \text{then the leakage rate constant } r \\ = -0.0358 = -0.0825 \\ 0.4343 \end{aligned}$$

Substituting this value, and the values C = 50 ppm and C₀ = 2000 ppm into the equation

$$\begin{aligned} C &= C_0 (1 - e^{-rt}) \\ 50 &= 2000 (1 - e^{-0.0825t}) \end{aligned}$$

$$\begin{aligned} \text{we can calculate that } t &= 0.307 \text{ mins.} \\ &= 18.4 \text{ secs.} \end{aligned}$$

Similarly the time taken for the model C, D, and A goggles to reach 50 ppm is 12.5, 11.3, and 5.9 secs. respectively.

Conclusion

Of the goggles tested, the Model B is the best in terms of both user comfort and protection afforded. The Model A is the worst in terms of protection afforded, and second in terms of user comfort.

However, the protection afforded by the Model B goggle is not good. Table 15 shows that 50% of the user population will have a leakage half-time which is less than 8.4 minutes. In more practical terms, 50% of the Model B goggle user population will exceed 50 ppm of H₂S in the eye cup in less than 18.4 secs., when the environmental

concentration is 2000 ppm.

50% of the users of Model C, D, and A goggles will reach 50 ppm of H_2S in their goggles, when the environmental concentration is 2000 ppm, in times shorter than 12.5, 11.3 and 5.9 secs. respectively.

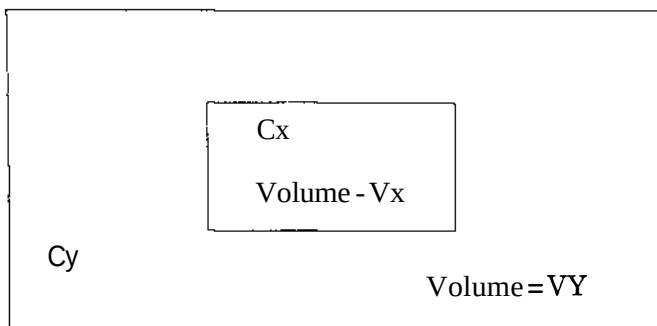
References

- 1) *Environmental Health Criteria 19 Hydrogen Sulphide* World Health Organization 1981.
- 2) F.R. Engelhardt, M.G. Holliday, *Dose Response Relationships of Acute Exposure to Sulphur Dioxide* May 1981. Report prepared by M. Holliday and Associates for the Atomic Energy Control Board, Ottawa, Canada.
- 3) *User Requirements for an Emergency Respirator* for B.H. W.P.
- 4) Samuel Gladstone, the Kinetic Theory of Gases. *Elements of Physical Chemistry* MacMillan and Co. Ltd. 1954.
- 5) R.A. da Roza, C.A. Cadena-Fix et al. *Reproducibility of Respirator Fit as Measured by Quantitative Fitting Tests*. Am. Ind. Hy. Assoc. J. 44(11) 788-794 (1983).
- 6) *Calculator Decision Making Source Book*. Texas Instruments Inc. 1977.
- 7) A. Hack, E.C. Hyatt, B.J. Held et al. *Selection of Respirator Test Panels Representative of U.S. Adult Facial Sizes*. LA 5488. Los Alamos Scientific Laboratory, Los Alamos, N.M. (1971).
- 8) J.R. King, *Probability Charts for Decision Making* Industrial Press Inc., 1971.

APPENDIX 1

Mathematical Model of Gas Leakage Out of and Into Protective Goggles

Prepared by: D. Agnew
- SSD-Pickering



An enclosed space of volume V_X is placed within a space of volume V_Y .

The concentration of gas in V_X is C_X and in V_Y is C_Y .

The enclosed space of volume V_X is leaky.

Let us look at what happens to the concentration of gas in the inner volume V_X .

The number of particles of gas entering V_X from V_Y in time dt is $dN_{X_i} = \lambda^1 C_Y dt$

(λ^1 = proportionality constant having units of volume/time)

The number of particles of gas leaving V_X in time dt is $dN_{X_o} = \lambda^1 C_X dt$

The net increase in the number of particles in V_X in time dt is $dN_X = \lambda^1 (C_Y - C_X) dt$

Therefore, the increase in concentration of gas in V_X in time dt will be

$$\frac{dN_X}{V_X} = dC_X = \frac{\lambda^1}{V_X} (C_Y - C_X) dt$$

or

$$dC_X = \lambda (C_Y - C_X) dt$$

(λ is the proportionality constant having units of time^{-1})

Case 1

Gas Leaking from V_X into V_Y

Suppose at time $t = 0$ $C_Y = 0$

If $V_Y \gg V_X$ then $C_Y = 0 = \text{constant}$

$$\therefore dC_X = -\lambda C_X dt$$

$$\frac{dC_X}{C_X} = -\lambda dt$$

C_X

Integrating both sides we get

$$\ln C_X = -\lambda t + k$$

$$C_X = e^{-\lambda t} e^k$$

If $C_X = C_0$ at $t = 0$ (boundary condition)

$$C_0 = e^k$$

$$\therefore C_X = C_0 e^{-\lambda t}$$

Case 2

Gas Leaking from V_Y to V_X

Suppose at time $t = 0$ $C_Y = C_0$

Since $V_Y \gg V_X$ $C_Y = C_0 = \text{constant}$

$$\therefore dC_X = \lambda (C_0 - C_X) dt$$

$$\frac{dC_X}{(C_X - C_0)} = -\lambda dt$$

$(C_X - C_0)$

Integrating both sides we get:

$$\ln (C_X - C_0) = -\lambda t + k$$

$$C_X - C_0 = e^{-\lambda t} e^k$$

If $C_X = 0$ at $t = 0$ (boundary condition)

$$0 = C_0 + e^k$$

$$\text{or } e^k = -C_0$$

$$\therefore C_X = C_0 (1 - e^{-\lambda t})$$