CARBON MONOXIDE POISONING AND AN IMPROVED METHOD OF ITS SPOT DETECTION

D. P. RAJWAR AND A. K. GHOSH

Central Mining Research Station, Dhanbad

(*Received* 29 *Dec.* 1965, *revised* 31 *Aug.* 1966)

The paper reviews some investigations on carbon monoxide poisoning and describes a detailed method for spot detection of carbon monoxide. A comparative study indicating the scope, limitation and range of the various other methods of spot detection has also been given.

Among the industrial toxic gases, the most frequently occurring is carbon monoxide. The highly poisonous gas is the product of incomplete combustion of carbonaceous matters and therefore may occur in different proportions in air at almost every place of human activity, particularly in and around coke-oven plants, garages, mines, sewage-treatment plants, hangars, factories and many other installations where fuels of organic origin are burnt. Large number of people succumb to carbon monoxide poisoning every year. The coal mine explosions claim more victims through carbon monoxide poisoning than from the explosions themselves. A large number of accidental deaths and suicides are also reported through the absorption of carbon monoxide present in the illuminating gas. In 1946 in New York City alone there were 268 suicides and 281 accidental deaths by carbon monoxide poisoning[1]. Since carbon monoxide constitutes one of the products of explosives used by military personnel as well, the danger to the defence forces poisoned by it during peace time manoeuvres as well as in war cannot be under estimated. The necessity of spot detection in the fields of civic and military activity can not, therefore, be over tressed. Table 1 shows the extent to which this poisonous gas may be present at different places[2].

POISONOUS NATURE OF CARBON MONOXIDE

Carbon monoxide has an affinity for haemoglobin of blood equal to about three hundred times that of oxygen and the inhalation of the gas results in the almost quantitative formation of carboxy-haemoglobin in the red blood corpuscles. The formation of this compound in the blood incapacitates the systm to take up oxygen and relatively low level of atmospheric carbon monoxide may cause serious poisoning. Prolonged exposure to an air containing carbon monxide as low as 0·15% may prove fatal. Two different modes of attack can be distinguished in carbon monoxide poisoning :

1. Formation of carboxy-haemoglobin by carbon monoxide through the displacement of oxygen. The envelope of the blood corpuscles are not damaged and red corpuscles remain unchanged.

2. The internal vesicular respiration is inhibited by carbon monoxide where the function of the respiratory enzyme is paralysed in a similar way to that in cases of poisoning with hydrocyanic acid gas or hydrogen sulphide. In the latter the toxic gases combine with

TABLE 1

CARBON-MONOXIDE CONTENT

Type and Surce	%Co by volume
Explosion in an experimental mine immediately after dust explosion	8·0
Mine explosion, one day after explosion in an experimental coal mine	1·0
Mine fire	1·0
Blasting with 40% gelatine dynamite, 7 minutes after shooting 100 sticks	1·2
Blasting products of combustion :	
Black blasting powder	10·8
40% nitroglycerine dynamite	28·0
40% ammonia dynamite	5·0
T. N. T.	60·0
Blast-furnace stack gas	28·0
Bessemer-furnace gas	25·0
Crucible furnace, gas fuel melting Al-Cu Sn alloy	5·5
Arc furnace melting aluminium	32·2
Cupola gas	17·0
Coke-oven gas	6·0
Coal gas	16·0
Carburreted water gas	30·0
Blau gas (cracked heavy oils)	40·0
Producer gas from coke	25·0
Distillation coal gas mixture	7·4
Producer gas from oil	5·0
Fuel gas	30·0
Gas range burning natural gas	0·2
Room heater burning natural gas	0·5
Automobile exhaust gas (average of tests of 100 cars of all types)	7·0
City fire (black smoke from burning buildings)	0·1
Insulation burning in electric arc	0·5
Furnace gas of small-house heating and hot-water system	1·0
Railroad-locomotive stack gas	2·0

the trivalent iron (Fe^{3+}) and prevent its reduction, whereas in the case of poisoning by carbon monoxide, bivalent iron (Fe^{2+}) of the respirarory enzyme reacts with the gas and thereby inhibits its participation in the oxidation process. The relation[8] of the carbon monoxide contained in the haemoglobin ($CO\text{-}H_b$) to the atmospheric carbon monoxide concentration as well as the duration of exposure is illustrated in Fig. 1. The threshold or toxic value of carbon monoxide lies at about 0·02% and limiting fatal concentration at roughly 0·10%, both values being percentages by volume. A well defined carboxy-haemoglobin ($CO\text{-}H_b$) concentration corresponding to the maximum blood saturation level exists; the value depends upon the carbon monoxide level and the period of exposure, the latter being affected by the movements and nature of work of the subject. The carboxy-haemoglobin level in the blood stream of a man at work reaches roughly 20% at an atmospheric content of 0·25% carbon monoxide within an hour. The carbon monoxide absorbed in the human organism is stable and does not get oxidised to carbon dioxide. A certain part may be expelled together with the air exhaled and the elimination process that might go up to 24 hours is accelerated through increased partial pressure of the oxygen concentration in the blood vessel. No definite data, however, exists

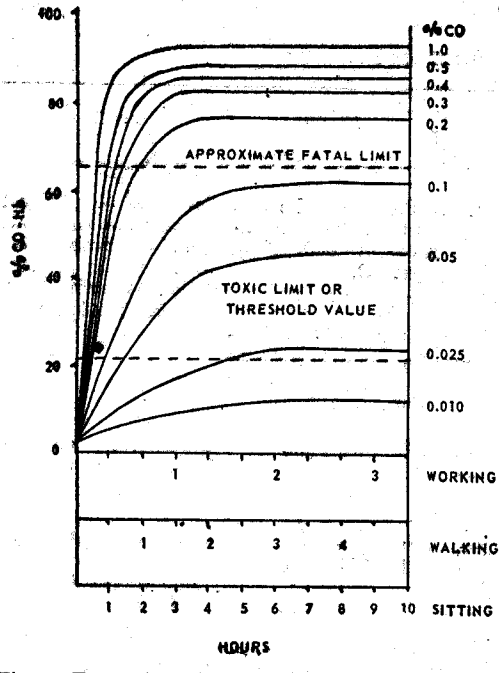

Fig. 1—The carboxy-heamogiobin in blood stream in relation to the time of exposure and the concentration of carbon monoxide in the atmosphere.

as to the possibility of cumulative carbon monoxide poisoning occurring as a result of prolonged exposure to carbon monoxide concentration of less than the threshold of toxicity value.

Physiological response and toxicity of carbon monoxide poisoning

Apart from the headache, dysponea, dizziness, nausea etc. frequent appearance of a pink-skin in cases with white subjects is commonly associated with the poisoning by carbon monoxide. The absence of such outward symptoms, however, does not necessarily exclude carbon monoxide as the source of poisoning.

Table 2 indicates the toxic effects of carbon monoxide concentration in atmosphere on individuals resting as well as doing physical work[4]. The effects are broadly agreed upon although minor variation in the findings in respect of the response of individual to toxic effect, has been reported [5, 6].

TABLE 2

EFFECTS OF CARBON MONOXIDE POISONING

Concentraion of carbon monoxide in air		Effect on individuals	
Parts per million by volume	mg./m³ (20°C)	Resting	doing physical work
50	58	Nil	Nil, unless exercise is very strenuous.
100	116	Nil	Perhaps slight headache and some shortness of breath after 2–3 hours.
200	232	Headache after 3—4 hrs.; symptoms do not become severe.	Headache; shortness of breath, dizziness, palpitation after two hours.
500	580	Headache, palpitation, nausea and dizziness; symptoms begin after 1—1½ hours.	Severe headache, dizziness of vision, possibly vomiting and collapse. Symptoms begin after 45 min to 1 hr.
1000	1160	Mild symptoms appear after 1—1½ hrs becoming servere after 2½ hrs with collapse; prolonged exposure may be fatal.	Mild symptoms after 30–45 mins severe symptoms after 45 mins. to 1 hr.
10000	11600	Mild symptoms after 10 mins. becoming severe in 15 mins. This concentration will be fatal if breathed for more than 2—3 hrs., and may be fatal in a shorter period.	Mild symptoms in 3–5 mins. becoming rapidly severe. Danger to life.

TABLE 3

METHODS FOR SPOT DETECTION OF CARBON MONOXIDE

Method and reaction	Type	Nature of test	Range	Remarks
1. (*a*) Canaries	Spot	Behaviour in movement.	(*a*) Positive indication with in 75—130 minutes in 1000—1200 ppm CO.	(*a*) Time interval between response of man and observable response of the animal is often not sufficent for use in practice.
(*b*) Japanese dancing mice	Spot	Do.	(*b*) Same in 5–10 minutes. Quicker response in highr concentrations.	
2. Palladous Chloride detectors (reduction to metallic Palladium).	Spot	Change in colour from Brownish yellow to black.	200—1000 ppm.	Sensitivity decreases with low air temperature.
3. CMRS Co-detector tubes Catalytic reduction of yellow ammonium silicomolybdate complex.	Spot	Change in colour from yellow to blue matched with permanently coloured gels.	10—1000 ppm. 1 ppm detected.	Interfering substances are strong reducing or oxidising gases present in very large amount.
4. NBS Indicator. Catalytic reduction of yellow ammonium silicomolybdate complex.	Spot	Change in colour from yellow to blue. Matched with printed strips.	10—1000 ppm	Matching may be affected subjectwise. Reducing and oxidising gases may also interfere.
5. Hoolamite detectors. Reduction of Iodine pentoxite to Iodine.	Spot	Colour of white granules change to bluish green, violet brown and finally to black	1000—10,000 ppm	Interfering gases are acetylene, ammonia, butylene, ethylene etc.
6. Blood method with pyrotannic acid	Laboratory and Spot	Light brownish grey suspension is formed. Matched with standerd colours.	Accurate in the range of 100—200 ppm. Maximum indication 2000 ppm.	Limited application due to difficulty in the preparation of standards with blood. Permanent standards may improve the utility of the method.
7. Haldane Caramine method	Laboratory	Caramine dye solution is added to a diluted blood to produce the tint of the poisoned blood.	Do.	Restricted use in caess of actual blood poisoning.

METHODS FOR DETECTION OF CARBON MONOXIDE

The methods of detection and estimation can be broadly placed into two major groups—the detection and estimation of carbon monoxide on the spot and estimation in the laboratory. Since the laboratory methods for the determination of carbon monoxide are well known, some of the important spot detection methods along with the ranges of detection and limitations are summarised in Table 3.

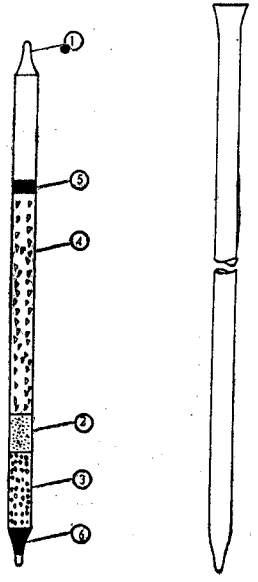

Fig. 2 - Detector tubes before and after filling.

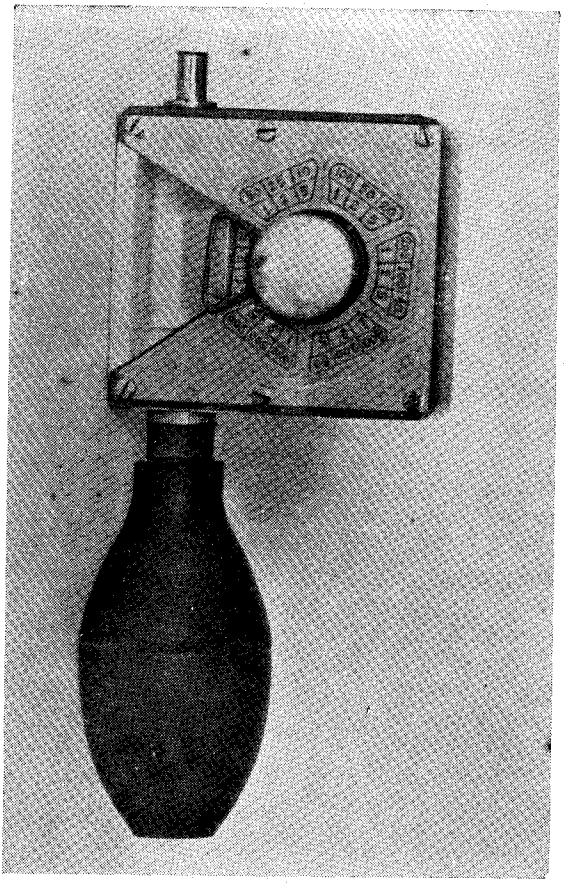

Fig. 3 –Aspirator-cum-comprator for carcon monoxide detector tubes.

Indigenous availability of the high grade silica gel prompted the authors to develop a method based on the colorimetric reaction of carbon monoxide with silico-molybdate complex. This method has been described here in detail. The technique employed in this method was developed in our laboratory[7].

AN IMPROVED METHOD FOR SPOT DETECTION OF CARBON MONOXIDE

Principle

The basic principle of the reduction of yellow silico-molybdate (Mo^{6+}) to lower oxides has been utilised in this method. A number of reducing agents (including Mo^{3+} and carbon monoxide) have been found to reduce molybdates into colloidal molybdenum blues[8], the composition of which approximate to $Mo_8O_{23}H_2O$. The stages of colour change (from yellowish green to green and finally to deep blue) are indications of the extent to which the reduction has been effected and thereby relates to the concentration of the reducing agent. Consequently, the reaction is not specific as hydrogen sulphide gas, unsaturated

hydrocarbons, moisture etc. also produce identical colour changes. These interfering gases can, however, be easily removed by employing suitable absorbents which do not absorb carbon monoxide to an appreciable extent.

Detector tube:

The carbon monoxide detector tube described here consists of a 14 cm. pyrex glass tube, of 7 mm. to 8. mm internal diameter (Fig. 2) and contains a short (1 cm.) column of silica gel impregnated with silico-molybdate co mplex. On either side of this yellow reagent column two short columns (about 4 cm. and 2 cm.) of guard silica gel remove the interfering gases and moisture by absorption. The gel columns in the tube are kept in position by plugs of glass cloth and the ends of the tube are vacuum-sealed with a pointed flame. In actual use the ends of the tubes are broken and the air sample to be tested is drawn through the tube by means of an aspirator—cum—comparator (developed at the Central Mining Research Station, Dhanbad)—see Figs. 3 and 4. Any colour change produced indicates the presence of carbon monoxide in the sample. This change in the colour of the reagent gel is matched against a set of standard coloured gels to give the carbon monoxide content directly from the scale. The comparator gels are prepared by impregnating silicagels with different admixtures of Prussian blue and Potassium dichromate solutions an drying them at 150°C. They are subsequently filled in pyrex tubes having the same diameter as the detector tubes.

Detailed procedure for preparing the dectector tubes is given below:

REAGENTS

(*a*) *Silica Gel for impregnation*

The gel to be used should preferably be of the non-indicating type and colourless. The sizes should be such that the entire amount passes through 60 B.S.S. sieve and retained on 72 B.S.S. sieve. Even if the purity of the gel is guaranteed by the manufacturers, it

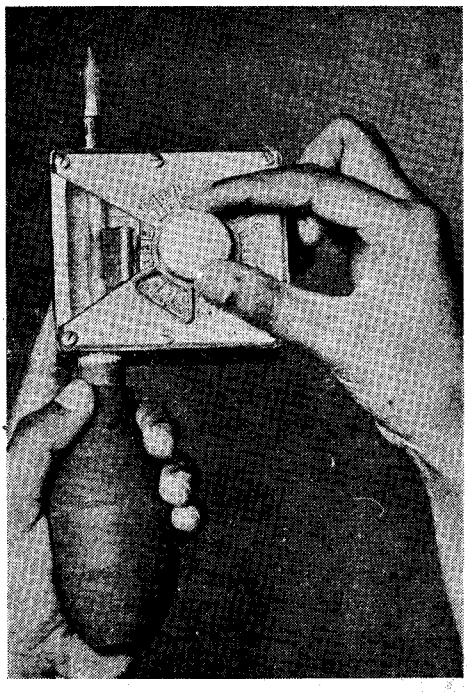

Fig. 4 Detecting apparatus in use.

Fig. 5 –Vessel for checking gel prior to use.

is necessary to purify it once more by digesting it in nitric acid and subsequently washing with distilled water. The possiblity of the size reduction during digestion and washing processes cannot be over ruled. It is, therefore, advisable to repeat the sieving operation after the purification. Further, the gels available in the market exhibit different activities depending on the mode of their preparation. The colour developing quality of silica gel may also be affected. It is, therefore, advisable to carry out the following experiments to test the gel for its suitability.

Testing the gel for its suitability;—5 gm. of the gel is boiled with excess nitric acid for half an hour and washed with distilled water several times to free it from acid. It is then dried at 110°C in an air oven for four hours. 2 gm. of this washed gel is transferred to 50 c.c. pyrex glass bottle and heated in furnace to a temperature of 340±20°C for four hours. The open and stopper (Fig. 5) containing silica gel is placed on it and allowed to cool. 5 ml of 5% ammonium molyb- date solution is added to the cooled gel followed by an addition of 4 drops of 50% sulphuric acid. The bottle is stoppered, shaken for two minutes and kept for 2 hours to allow the colour to develop. The coloured solution is extracted, made up to 100 ml. with distilled water and the intensity of coloration measured with the help of a spectral type photometer using one centimetre cell at 420 mμ. The gel suitable for the purpose should show an extinction of 0·60—0·65.

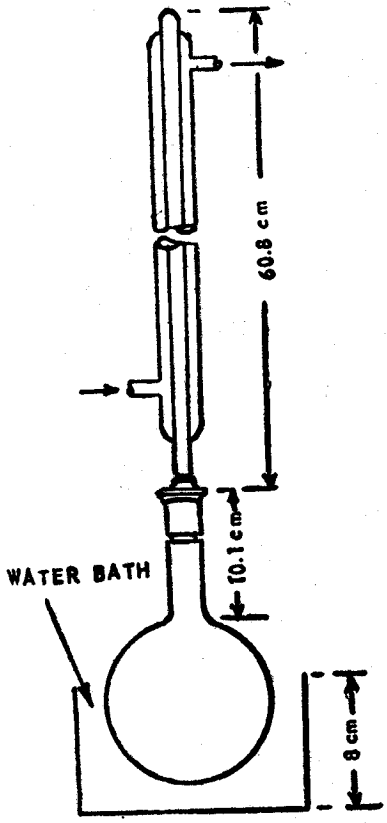

Fig. 6 - Reflux unit for the purification of gel.

Purification of the impregnation gel.— The gel thus found suitable is purified in the following manner: 500 gm. of the gel is dried at 320°C for two hours, transferred to a 2-litre flask and subsequently refluxed with nitric acid ona water bath (Fig. 6). Concentrated nitric acid (A.R.) covers the silica gel completely and the level of the acid stands 4 cm. above the surface of the gel. It is refluxed for 48 hours and the loss of acid is replenished by periodic addition of the acid. After 48 hours, the acid is siphoned out and the gel washed several times with re-distilled water till the wash water is rendered clear and has a *pH* value between 4·9 and 5·0 is obtained. About 30 times washing with 500 ml of Redistilled water each time and boiling for 10 minutes generally suffice. The washed gel is dried in an air-oven for six hours at 110°C and subsequently stored in clean 2-litre reagent bottles provided with ground glass stoppers. The stopper shouldbe ungreased and contact of the gel with rubber, oil grease or any other reducing material should be carefully avoided.

(*b*) *Guard gel*

The silica gel used for the guard gel employed in the detector tube for removing other reducing gases and moisture should also be colourless and non-indicating type. It should entirely pass trough a 30 B.S.S sieve. The purification of the gel is carried out in a manner similar to that of impregnation gel.

(*c*) *Polladous sulphate solution*

1 gm. of 99·9 % metallic palladium wire (0·5 mm. dia.) is cut in small pieces of 1 mm. length and dissolved completely in 20 ml. of 20% nitric acid contained in a 100 ml. pyrex conical flask. The solution is transferred to a clean porcelain basin, evaporated to dryness in a furnace cupboard and further heated in a furnace at 350°C for eight hours. The black shining residue is scrapped off and transferred to the 100 ml. pyrex conical flask. About 12 ml. of sulphuric acid is used in partially dissolving, and loosening the residue. Continuous boiling of the material with the acid on a hot plate and using an air condenser (Fig. 7) dissolves the black oxide of palladium and deep brown solution is obtained. 1 ml. of distilled water is added through the top of the condenser at regular intervals of 15 minutes during boiling and the addition is discontinued with the cessation of evolution of suplhur dioxide gas. The boiling is, however, continued for another half an hour. The palladium is estimated by dimethy glyxime method form a 2 ml. aliquot and the solution is accordingly diluted to give 0·015 gm. per ml. of palladium and 0·25 gm. of 36 *N* sulphuric acid.

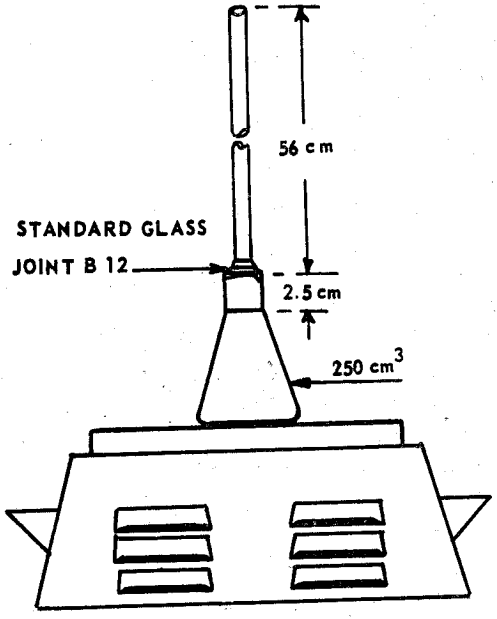

Fig. 7—Apparatus for preparation of Palladous sulphate solution

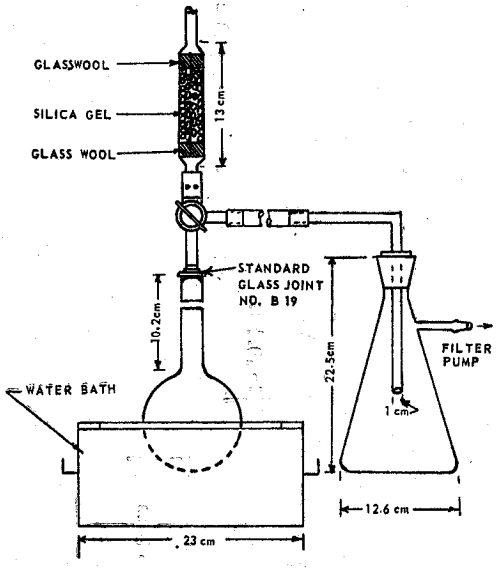

Fig. 8—Set-up for initial drying of gel after impregnation.

(*d*) *Preparation of ammonium molybdate solution*

15 gm. of A.R. quality ammonium molybdate is dissolved and made upto 200 ml. with freshly boiled distilled water.

Drying of gel prior to Impregnation:—500 gm of the purified gel is taken in a 2-litre pyrex glass flask fitted with a standard joint. The gel is heated for 4 hours at 340 ± 20°C in a suitable furnace under suction. In case there is already a furnace at hand, a suitably modified Pyrex glass vessel of appropriate size and fitted with standard joints may replace flask. In either case, the vessel must be provided with an open top stopper containing guard gel to prevent moisture from getting inside during cooling. After heating the stopper is replaced and the vessel allowed to cool.

(*e*) *Impregation*

The impregnation vessel should be a 2-litre pyrex flask, fitted vacuum tight points in the manner given in Fig. 8. The dried and cooled gel is transferred to the 2-litre flask and the reagents given below are added as quickly as possible :

Ammonium molybdate solution (7·5%)	100 ml.
Palladium sulphate solution (as prepared previously)	25 ml.
Distilled water	200 ml.

If the gel has already taken in some moisture, the development of yellow colour by the addition of the reagent may not be complete. In such case, the quality of the detector tube gels would not be reliable for detection of carbon monoxide. A pinch of the gel may be allowed to react with two drops of ammonium molybdate solution and a drop of 2% sulphuric acid on a glazed porcelain tile to test if the gel is dry enough. An intense yellow colour must be formed. Otherwise the gel should be dried again as described earlier. The yellow colour which is instantaneously formed is allowed to develop completely by keeping it overnight.

(*f*) *Initial Drying*

The flask containing the gel at the bottom and the yellow coloured silico-molybdate complex on the top is fitted to a set up as given in Fig. 8. The flask is connected to a vacuum pump via trap containing indicating type of silica gel dehydrated at 320°C. During the process of drying, the gel shows a tendency to cake, and the flask is occasionally taken out and struck gently against a thick and semi-hard rubber sheet in order to disintegrate the cakes formed. The rubber tube connecting the flask to the filtering conical flask should be sufficiently long (about 10 inches) to permit this operation.

When the cakes are disintegrated and the gel particles are dry enough to move freely with respect to each other (in actual process, the gels quiver, that is, a visual analogy to boiling is observed), the three-way stop cock is turned to the atmosphere, and the air allowed to enter into the flask through the guard tube. The flask is subsequently taken out, closed with a ground glass stopper and kept in a cool place.

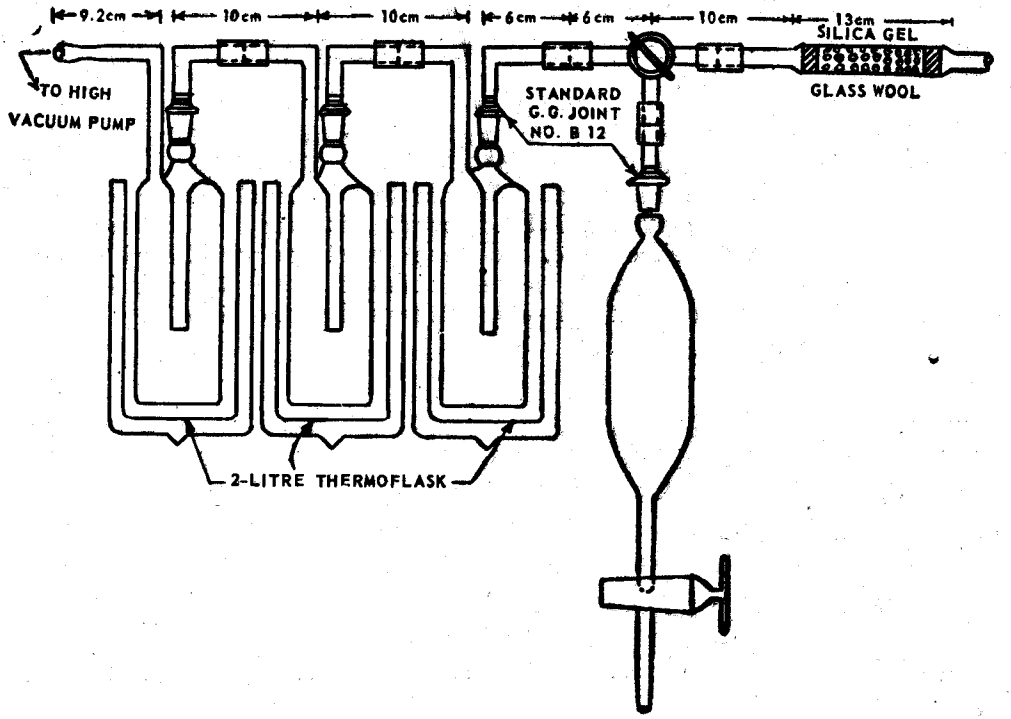

Fig. 9—Assembly for final drying of impregnated gel.

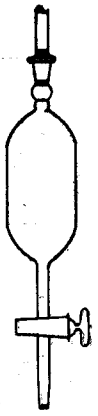

Fig. 10—Dosing apparatus for reagent gel.

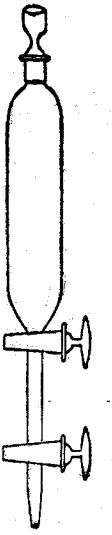

Fig. 11 - Dosing apparatus for guard gel

(g) Final Drying

The sensitivityof the impregnated gel for the detection of carbon monoxide is largely governed by its low moisture content and the gel is to be thoroughly dried to make it properly sensitive. Since it is very difficult to remove traces of moisture from silica gel, special drying technique is employed. The set up, found suitable by the authors, has been illustrated in Fig. 9. A high vacuum Cenco-pump (10^{-4} mm *Hg* and capacity 30/40 litres per minute) is employed for the purpose and system of traps filled with dry silica gel and kept in freezing mixture, fixes the moisture evacuated. Salt-ice mixture kept in thermos flask is used as freezing mixutre. Theremometers are placed in the bath and periodic replenishment of salt ice mixture assures a sufficently low temperature (—15°C).

A cylinderical or bulb type seperating funnel of 500 ml. capactiy (Fig. 10) is used both for final drying as well as dosing. No grease is applied to the stop cock and the filling in of the tubes is completed soon after drying.

Eight hours are generally required for final drying of 250 gm of impregnated and previously dried gel; the periodic measurement of the suction should not show a pressure higher than 10^{-3} mm. *Hg*.

(h) Filling up of the tubes

The moisture content of the reagent gel largely determines its sensitivity and, therefore, the gels should preferably be filled in the tubes immediately after final drying (same-day if possible) or kept in a big dessicator containing silica gel dehydrated at 340°C. The dosing tubes must be stoppered with thin film of Apiezon grease at the ends. The dosing stop cock, however, should preferably be left ungreased.

The filing in of the tubes is carried out in a room free from traces of unsaturated hydrocarbons or any other reducing vapouras. This is very important in the sense that traces of such gases might affect the sensitivity and spoil the product of the entire run. The relative humidity of the room where the filling in of the tube is carried out should not exceed 60% at 25°C. The tubes are rinsed and kept overnight in chromic acid and the glass cloth for pulgging is digested in nitric acid for four hours to remove any grease present on the materials. In either case, the traces of the acid are removed by repeated washing with distilled water and subsequent drying.

The guard gel to be filled is also dried at 340°C under vacuum for four hours and kept stored in the air-tight glass-stoppered bottle using a little Apiezon grease. Before pouring in the dosing bottle, the grease is removed with a piece of clean cloth.

The dosing vessels in Figs. 10 and 11 containing the freshly dried guard gel and the impregnation gel are kept vertical in two separate stands. A piece of square glass cloth is plugged inside the tube through the open end. A fixed volume of guard gel is first dosed in the tube. Impregnated gel is subsequently added by rotating the stop cock through 180° and another column of guard gel is finally added on the top of the impreguated gel. The entire column is pushed to 9·5 cm. from the lower end of the bottom gel by means of a stainless steel rod. One cm square of glass cloth is subsequently rammed in position and the tube immediately sealed by drawing it under vacuum with the help of a pointed gas flame. Storage ranging from 15 days to one month is advisable in case of tubes showing low initial sensitivity.

REFERENCES

1. Jaccobs, M.B., "The Analytical Chemistry of Industrial Poisons, Hazards and Solvents". 2nd Edition 1 (1949), p. 405.

2. *ibid.*, p. 402

3. HETZEL, K.W., *Brennstoff Chemie.*, 40 (1959) 115-122

4. Leaflet No. 7 (3rd Edition) H.M.S.O. (1955).

5. FREDRICK F.C., *Analyst.*, 56 (1951), 561.

6. HENDERSON, Y. & HAGGARD, H.W., "Noxious gases" (Reinhold, New York) (1943), 168.

7. GHOSH, A.K., RAJWAR D.P. & BAKSI, B., Indian Patent No. 78780, 7th October (1961).

8. SCHIRMER, F. B., AUDRIETH, L. F., GROSS, S. T. Meclellan and Seppi *L. J., J. Amer Chem. Soc.*, 64 (1942), 2543.