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Note

Measurement of sulphur hexafluoride with a Beckman electron capture detector in pulmonary clearance*

CHR[illegible]AN M[illegible]ERKS

Institu[illegible]che Interdisciplinaire en Biologie Humaine et Nucléaire and Institut de Recherches Cardiologi[illegible]pital Saint-Pierre, 1000 Brussels (Belgium)

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A method has recently been developed for measuring the distribution of the pulmonary ventilation–perfusion relationship involving the analysis of the pulmonary clearance of inert gases with various solubilities in blood[1–3]. The gases comprise two groups, firstly ethane, cyclopropane, halothane, diethyl ether and acetone, which are determined with a flame ionization detector (FID), and secondly sulphur hexafluoride, which is determined with an electron capture detector (ECD) (response ratio ECD/FID, of sulphur hexafluoride = 10^6).

The precise measurement of sulphur hexafluoride in the samples is important, as it enables the value of the physiological shunt to be obtained. Moreover, certain sulphur hexafluoride concentrations are near the limit of detection of the ECD. Also, the ECD is a very sensitive detector, but is also very delicate.

This paper describes a study of the various factors that influence the ECD response and the handling of the samples to be measured.

EXPERIMENTAL

Sulphur hexafluoride measurements were made with a Beckman GC 72-5 gas chromatograph. Gas samples were introduced via a 2-ml constant volume valve. The column was 6 ft. × 1/8 in. I.D. and was filled with Porapak T, 80–100 mesh, with helium as carrier gas. The Beckman ECD does not use a radioactive source, but low-energy electrons are emitted from a discharge in pure helium in a region adjacent to the sample chamber. A small amount of carbon dioxide absorbs radiation in the far ultraviolet region, which is emitted by helium atoms and which is capable of ionizing eluting compounds[4]. The flow-rate of discharged pure helium is 100 ml/min. The standing current, stability, noise and variation of retention time and of resolution of the sulphur hexafluoride peak were studied according to the carbon dioxide flow-rate, the polarizing voltage, the temperature of the column and the carrier gas flow-rate.

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In order to study the sensitivity of the ECD under various conditions, samples of the same concentration giving a peak of about one third of the standing current were used, and relative peak heights (R.P.H.) (the ratio between the height of the sulphur hexafluoride peak and the height of the standing current at the same sensitivity of the recorder) were measured.

RESULTS

Influence of carbon dioxide flow-rate on the noise and on the standing current

For a given polarizing voltage, the carbon dioxide flow-rate has an ideal value corresponding to a maximum standing current and minimum noise (Fig. 1). For very low carbon dioxide flow-rates, the standing current is very low but the noise decreases and disappears at a carbon dioxide flow-rate of zero. The detector no longer operates as an ECD but as a helium ionization detector. The peaks so obtained have a polarization inverse to those obtained in the ECD.

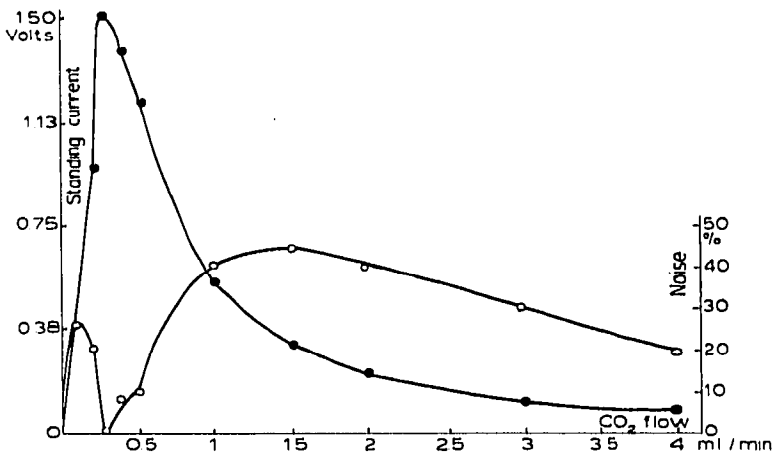

Fig. 1. Variation of standing current (●) with carbon dioxide flow-rate. The standing current varies from 0–1.5 V when the flow-rate increases from 0–0.4 ml/min. The noise (○), measured peak to peak, is expressed as a percentage of the standing current. Polarizing voltage, 500 V; flow-rate of discharged helium, 100 ml/min; column temperature, 70°; carrier gas flow-rate, 30 ml/min.

Stability of the standing current

The standing current increases when the polarizing voltage increases with a deflection, at *ca.* 400 V, where the shift of the standing current is minimum. To find this deflection (Fig. 2a), the carbon dioxide flow-rate must be altered; it varies from about 0.1 ml/min for a polarizing voltage of 100 V to 0.4 ml/min at 900 V. It is important to choose a suitable carbon dioxide flow-rate when measuring the deflection, otherwise the curve obtained might not show a deflection or might show one at an inadequate voltage (Fig. 2b).

The relative peak height is at a maximum at 400 V. For a low polarizing voltage (100 V) the R.P.H. is 80% of the maximal R.P.H.; at 300 V, it increases to 94%; at 500 V, it decreases to 88% while at 900 V it is 75% of the maximal R.P.H.

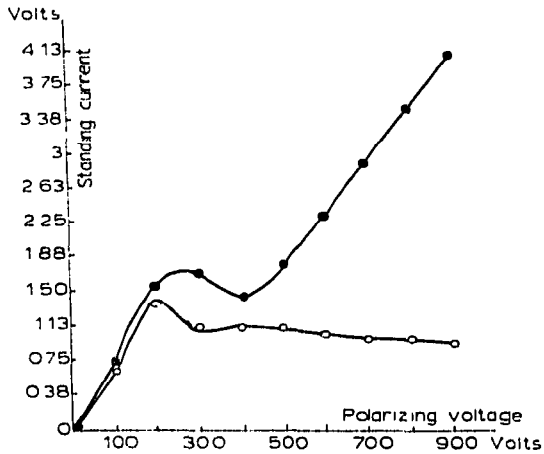

Fig. 2. Variation of standing current with polarizing voltage. ●, Carbon dioxide flow-rate adjusted for each measurement; ○, carbon dioxide flow-rate constant at 0.2 ml/min for all measurements.

Variation of the retention time and of the resolution according to the column temperature and the carrier gas flow-rate

As the gas samples are contained in glass syringes, the analyses should be carried out as soon as possible in order to reduce to a minimum the error due to leakages, so that the retention time must be short but the resolution of the sulphur hexafluoride peak with air peak must be good. Column temperatures from 23–110° and carrier gas flow-rates from 20–80 ml/min were tested. The polarizing voltage remains at 400 V and the flow of carbon dioxide is regulated so as to give minimum noise.

The resolution is good when the column temperature is 23°, whatever the carrier gas flow-rate, but the retention time is 5 min 24 sec for a flow-rate of 20 ml/min and 2 min 36 sec for a flow-rate of 80 ml/min.

For the other column temperatures, the retention time is good and increases from 36 sec–1 min 45 sec for carrier gas flow-rates from 50–20 ml/min. The resolution is good for column temperatures from 50–90° but poor at 110°. The relative peak height is maximal for a column temperature of 70° and a carrier gas flow-rate of 30 ml/min.

Handling of the samples

The blood samples are stabilized by the gas phase (*e.g.*, helium) and the latter is analysed. A detailed explanation of the handling is given elsewhere[5]. However, the following points must be stressed.

Sulphur hexafluoride is very soluble in fats so that the gas samples must be preserved in ungreased gas-tight glass syringes of 50-ml volume. The sulphur hexafluoride concentration decreases by approximately 3% per hour because of leakages.

It is well known that the ECD response is not linear, as the peak obtained corresponds to a reduction in the standing current due to capture of electrons by sulphur hexafluoride. It is advisable never to have a deflection greater than half of the standing current in order to retain good sensitivity. Some samples are diluted up

to 2000-fold and it is then important to take into account the dead space, which is about 0.6 ml for a 50-ml syringe. Thus, when a syringe originally containing a sample of sulphur hexafluride up to the 5-ml calibration mark is filled with helium up to the 50-ml calibration mark, the dilution factor is about 9 and not 10. The diluted sample must then be either analyzed immediately or transferred into a clean syringe, because the loss of gas from the walls of the syringe after a large dilution may result in errors of up to 10%, 30 min after the dilution has been made.

Again, because of the non-linearity of the response, a calibration graph must be constructed. The sample that gives the highest peak is taken as a starting point then diluted with helium to three quarters of its initial concentration. The resulting sample is analyzed, diluted again to three quarters of its preceding concentration, and so on until the whole range of samples to be analyzed is covered, *i.e.*, a dynamic range of 10^{-8}–10^{-10} ml/ml. The heights of the peaks of the samples analyzed are drawn on the graph obtained in order to determine the correct relative concentration. The dilution graph must be drawn as soon as possible so as to avoid errors due to gas leakages.

CONCLUSION

The conditions chosen in order to obtain good resolution with a minimum retention time are: column temperature, 70°; carrier gas flow-rate, 30 ml/min; polarizing voltage, 400 V; carbon dioxide flow-rate, adapted for minimum noise.

Provided that the above precautions are taken, the analysis of the samples by gas chromatography is very sensitive and reproducible. The dynamic range of the ECD for sulphur hexafluoride is 10^{-8}–10^{-10} ml/ml. If precise dilutions are made, avoiding the phenomenon of gas leakage, and taking the dead space of the syringe into account, this range can be much larger and still give accurate results. Six samples from the same blood syringe were analyzed and the standard deviation of the measurements was 2.8% of the mean.

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