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ESTIMATING METHANE EMISSION USING SF6 TECHNIQUE IN RUMINANTS

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Abstract: Sulphur hexafluoride (SF_6) is the most common tracer gas used to estimate CH_4 production from the ruminants. This technique relies on a constant release of SF_6 from a bolus administered into the rumen of an animal. Gas samples are collected from around the nose and mouth of the animal via a harness and evacuated canister and these samples are then analysed using a gas chromatograph. The release rate of SF_6 from the bolus and the ratio of SF_6 to CH_4 in the breath sample are used to calculate the CH_4 emission from each animal. This method of estimating CH_4 emissions has the advantage that individual grazing animals can be measured, as well as groups of animals simultaneously. It is also a relatively cheap method for measuring CH_4 emissions, although the cost of purchasing a gas chromatograph capable of measuring SF_6 in parts per trillion is considerable.

Introduction

This method is relatively new and was first described in 1993–1994. The main purpose of the method was to investigate energy efficacy in *free ranging cattle*, because it had been queried that results obtained in respiration chambers could not be applied to free ranging animals. The basic idea behind the method is that methane emission can be measured if the emission rate of a tracer gas from the rumen is known. For this purpose a non-toxic, physiologically inert, stabile gas is needed. Furthermore, the gas should mix with rumen air in the same way as methane. SF6 was chosen, because it fulfills the above criteria, cheap, has an extremely low detection limit and is simple to analyze.

Principle

The SF6 measurement technique measures the rate at which cattle release methane using a tracer technique. A permeation device that release SF6 at a known rate is placed in a cow's rumen. The animal is fitted with a sampling system such that ambient air from around the mouth and nostrils can be collected over an extended period of time. The air sample is

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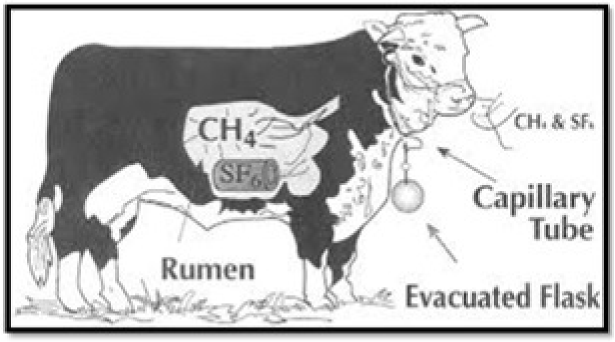
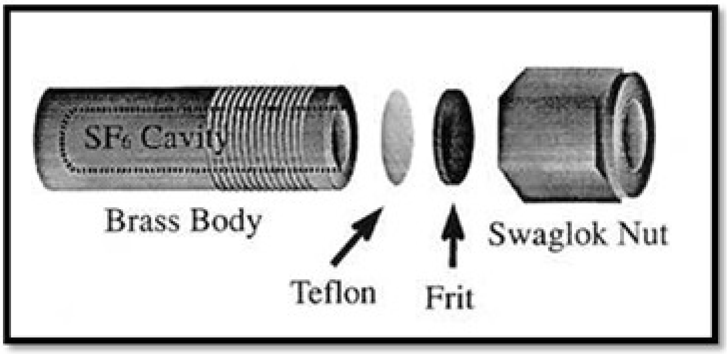
then analysed for methane and SF6 and these concentrations along with the known release rate allow calculation of the methane emission rate.

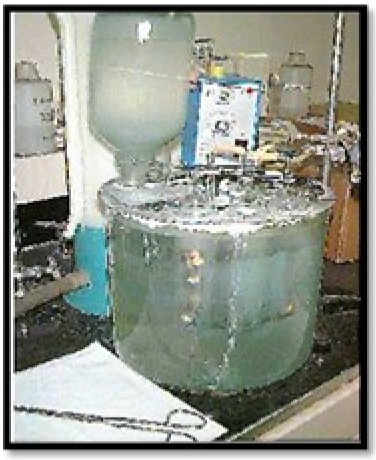


Components of the system

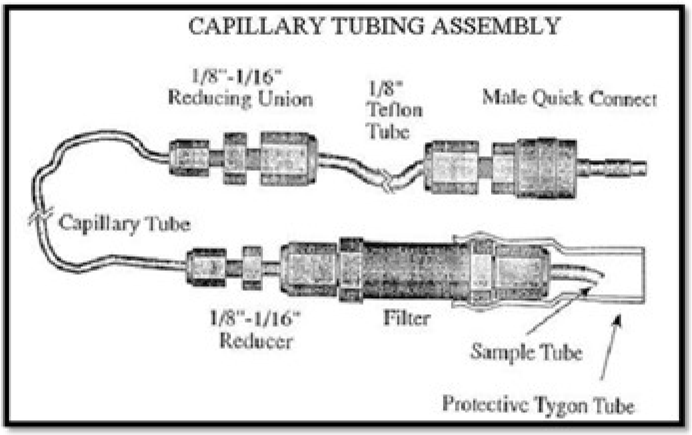
The components of the system include a permeation device placed inside the rumen a halter that fits snugly around the cow's head, a PVC yoke that fits over the neck, capillary tubing for air transfer, a gas dilution system, and gas chromatographs for methane and SF_6 determination.



To charge the permeation tube with SF6 the nut, Teflon window and frit are removed followed by immersion of the tube body in a cryogen such as liquid nitrogen. After the tube has reached the cryogen temperature, it is removed and any liquid is poured out of the cavity. The cavity is then quickly filled with SF6. The filling is accomplished by withdrawing about 60 cc of gaseous SF6 is each of two plastic syringes. The needle is placed in the cavity of the could permeation tube body and the plunger is slowly depressed by transfer the gaseous SF6 into the permeation tube body cavity. The tube is quickly capped with Teflon window, frit and nut following completion of the SF6 transfer. The permeation device is then weighed. This procedure should provide a tube containing about 600mg of SF6.

The tube should then be placed in a glass receptacle, in a 39◦C water bath. A small flow of clean N_2 gas is maintained to purge the glass receptacle of SF6 emissions. Weights of each tube should be taken weekly to determine the release rate of SF6.Five to six weeks is generally required to gain a goof idea of the release rate.

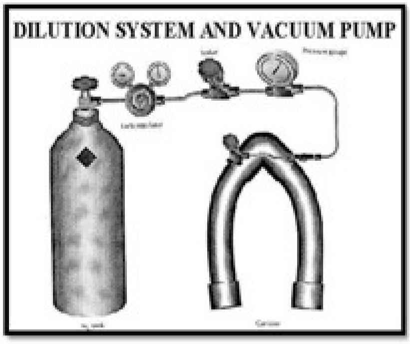


The length of the capillary tubing regulates the sampling rate. Stainless steel capillary tubing with an inside diameter of .005" and an outside diameter of 1/16" serves as the flow restrictor and transfer line. Short sample integration periods (e.g. 1 hr) may require only a short piece of tubing while longer periods (e.g.24 hr) require much longer lengths of tubing.

After assembling the PVC pieces, and allowing the glue to dry (12-24hr), place the entire assembly into a 120 – $135^{0}C$ oven for 5-10min. Keep checking the pipe by squeezing it until it is soft and pliable. Remove the pliable pipe and bend the legs into the desired position such that it should fit with cow's neck.

Now install the gas sampling valve. After assembly, the canister can be checked for leaks by pressurizing it with compressed air or nitrogen to 40 psi and then submerging it in water to watch for bubbles.

A vacuum pump is required to evacuate the canister, a pressure gauge is necessary to measure the pressure after filling with a gas sample, and a dilution system is necessary to pressurise the sample with nitrogen gas. In order to begin sampling a collection canister should be evacuated. Any vacuum pump capable of reducing the pressure in the canister to a few Torr is acceptable. After closing the valve on the canister, it is then ready to use.



After the sampling collection period has been completed, the canister taken off the animal and connected to the dilution system and the final pressure recorded. Nitrogen is then slowly added until the pressure in the canister is increased to about 1.2 ATM. Another pressure reading is recorded to calculate the dilution factor. With the contents of the canister under positive pressure, it is easy to transfer an aliquot of sample to the GC system. The canister can be attached directly to the gas sampling valve in the GC via quick connect fittings. Simply opening the canister valve will then allow sample transfer to the fixed volume loop on the GC.

GAS ANALYSIS

Methane concentration in the sampling canister is determined by gas chromatography. SF6 is measured using a gas chromatograph equipped with an electron capture detector.

CALCULATIONS

The tracer method utilizes SF6 to account for dilution as gases exiting the cow's mouth mix with ambient air. It is assumed that the SF6 emission exactly simulates the CH4 emission; thus, the dilution rates for SF6 and CH4 are identical. Mixing due to turbulent diffusion is much more important than molecular diffusion in the atmosphere. Similarly, gas transport from the rumen out of the mouth is dominated by forceful contractions and eructation so that molecular emission rate (Q_{CH4}) can then be calculated from measured CH4 and SF6 concentrations and the known release rate of SF6 (Q_{SF6}):

$(Q_{CH4})= (Q_{SF6}) \times [CH_4]/ [SF_6]$

Background concentrations of methane and SF6 should be subtracted from the concentration of these species measured in the collection yoke. The background SF6 concentrations are normally very small compared to yoke concentrations and therefore can usually be neglected. However, background methane level (˜2 ppm; $[CH_4]_b$ should always be substracted from the methane concentration measured in the yoke ($[CH_4]_y$);

$(Q_{CH4})= (Q_{SF6}) \times ([CH_4]_y-[CH_4]_b)/ [SF_6]$

Procedure in short:

- SF6 is filled into *small permeation tubes*.
- The rate of diffusion of SF6 out of the permeation tubes is measured by placing them in a 39 °C water bath and measuring the daily weight loss until it is stable.
- The permeation tube is then placed in the rumen of an experimental animal and collection of air can start.
- The sampling apparatus consists of a collection canister, a halter and capillary tubing. The capillary tubing is placed at the nose of the animal and connected with the evacuated canister.
- The tubing regulates the sampling rate. The sampling time is typically **one day**.

- The concentration of SF6 and CH4 in the canister is determined by *gas chromatography*. The methane emission is calculated from the release rate of SF6 and concentration of SF6 and CH4 in the containers in excess of background level as described above.

Results based on direct measurements of gas composition in gas head space in the rumen of canulated animals.

Uses:

To investigate nearly all aspects of feeding and nutrition

- e.g., level of feeding,
- effect of feedstuff,
- effect of chemical and physical composition,
- restricted versus ad libitum feeding,
- different additives and grazing.

Problems/Limitations:

Maintaining a ***constant release rate*** from permeation tubes.

- The release rate is important and will affect emission estimates if not correctly determined. The release rate from permeation tubes is determined under laboratory conditions by weighing the permeation tubes regularly for at least 1½ months. Only highly linear permeation tubes are used ($R2 > 0.997$). Tests of permeation tubes pre- and post-experiments have also shown differences in permeation rate. The permeation tubes are weighted in a laboratory in dry air and the release rate should be the same in the rumen. However, a 6–11% lower release rate in tubes placed in rumen fluid than in air has been observed.
- Effect of release rate upon emission rate of methane
- Permeation tubes with high release rates give higher methane emissions than tubes with low release rates. It is therefore recommended to use permeation tubes with nearly the same release rate when comparison of different treatments is needed
- Background level determination
- The measured concentration should be corrected for background levels of both SF6 and CH4. Measuring a representative background concentration under field condition can be difficult, because wind direction and other animals in the field can affect the concentrations.
- Inconsistency between methane measurements determined in chambers and with SF6 and within and between animal variation.

- Johnson et al. observed a 7% lower methane emission with the SF6 technique than with chambers with cattle, and this can partly be explained by the few percent of methane, which is lost via rectum. Comparisons also showed a slightly lower emission (5–10%) with the SF6 technique than with chambers for both cattle and sheep. However, others have shown slightly higher values with the SF6 technique than chambers, and yet other studies have found much higher values with the SF6 technique than chambers.
- Both within and between animal CV is much higher in experiments with the SF6 technique than with the chambers.
- In a study by Pinares-Patiño et al. the same animals were measured both with the SF6 technique and in chambers. The within CV was 4.7, 13.5 and 11.7% in chambers, with SF6 and with SF6 in chambers, respectively. Also the between animal CV was twice as high with the SF6 technique as with the chambers. The correlation between the different methods is also inadequate. Both the higher within and between animal variations increase the number of measuring days and number of animals needed to verify differences between treatments.

Conclusion

The SF6 method gives more variable results of methane emission than chamber measurements. This increases the number of animals needed to prove treatment differences. The ability to use the method to quantify the methane emission has been debated in a number of studies, but the technique is still new and further investigation can hopefully improve the technique. The method is the only available method for measuring individual free ranging animals on e.g., pasture.

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