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PERFORMANCE OF A MONITOR FOR ATMOSPHERIC METHANE MEASUREMENTS

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The performance of a Shimadzu gas chromatograph, model GC-14A, installed at INPE, São José dos Campos, Brazil, was evaluated as a monitor for atmospheric methane. The system uses two stainless steel columns, a FID detector and two valves in the injection and back flush operation. The retention time of the methane in the molecular sieve column is about 1.8 min. The precision of the system was 0.66%. The reproducibility test showed that the results are within the above uncertainty margin. Excellent linearity of the measured responses was obtained in the range of 1500 to 2500 ppbv, which is closest to the clean air concentrations to be expected from samples of remote areas. Several analyses of air samples especially collected at different ecosystems are also reported.

DESEMPENHO DE UM SISTEMA DE MEDIDAS DE METANO ATMOSFÉRICO *Descreve-se uma avaliação rigorosa do desempenho de um cromatógrafo a gás Shimadzu, modelo GC-14A, instalado no laboratório de ozônio do INPE, em São José dos Campos, Brasil, projetado especialmente para medir a concentração de metano na atmosfera. O sistema usa duas colunas de aço inoxidável, um detetor DIC e duas válvulas para o sistema de injeção e retrofluxo. O tempo de retenção de metano na coluna de peneira molecular é de 1,8 minutos. A precisão do sistema é de 0,66%. A capacidade de reprodução foi testada e mostra que os resultados estão dentro da faixa acima. As respostas medidas indicam excelente linearidade na faixa de 1500 a 2500 partes por bilhão, por volume (ppbv), que é a faixa mais próxima esperada nas amostras de ar limpo de regiões remotas. Outras análises de amostras especialmente coletadas em diferentes ecossistemas são comparadas entre si.*

INTRODUCTION

Gas chromatography using FID (Flame Ionization Detector) is a well-known technique to measure hydrocarbons, in general, and methane in particular. Methane, in spite of being the most abundant hydrocarbon in the atmosphere, with a typical concentration of about 1700 ppbv (parts per billion by volume), needs to be detected and measured with high precision, since very small variations are expected between

samples of different ecosystems, and long term variations or trends are typically around 1% per year (Rasmussen and Khalil, 1981; Steele et al; 1987). This paper presents test results of a system capable to respond to this challenge.

INSTRUMENTATION

A Shimadzu gas chromatograph, model GC-14A, was installed in the beginning of 1992 at the Ozone Laboratory of the Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brazil. The chromatograph is equipped with two stainless steel columns of 1/8" diameter. The first, 2.5m long, is packed with silicagel (60-80) mesh, and the second packed with molecular sieve 5A, (60-80) mesh is 3.0m long. The sample injection subsystem consists of a 10 port VALCO valve, connected to a 2.2 ml sample loop, and a second valve, 4 port, is used to select either sample or calibration gas (Fig. 1). The columns are operated at 100°C. The 10-port valve is triggered automatically by a relay.

As mentioned, the system uses a Flame Ionization Detector (FID) to detect the methane gas. The FID flame uses H_2, N_2, and air at flow rates of 30, 60 and 300 ml/min. respectively. The detector temperature is set at 120°C. During the analysis, the chromatogram is monitored on a video display, and the peak area (or height) is calculated automatically by a PC type data processor.

ANALYSIS PROCEDURE

The sample or calibration gas is injected into the sample loop when the ten port valve is in the LOAD position. It takes about 3 min. for the pressures to equalize, before the sample may be injected into the chromatograph. This is performed automatically, when the valve turns to the position INJECT. When in this position, the carrier gas N_2, at a flow rate of 60 ml/min. is forced to enter the sample loop, thus carrying the sample to the columns. While in column 1, CO_2 and H_2O are held by the silicagel and the CH_4 continues to column 2 after a retention time in column 1 of 2.2 min. CH_4 having left the first column, the 10 port valve is switched back to the LOAD position, in which the carrier gas flows in the reverse direction through column 1, carrying along the gases with higher retention times in the silicagel such as CO_2. This is the back flush operation which insures that components of higher retention times will not appear, after the CH_4 peak, in the chromatogram. Meanwhile, the CH_4 continues to flow through column 2, where its retention time is about 1.8 min. after which CH_4 is detected. It takes a total time of about 4 minutes between injection and detection.

In summary, the analysis sequence, in minutes, is:

Time 0: 10 port valve in position LOAD (This is also the back flush position for column 1). Sample loop is filled with sample (or calibration) gas.

Time 3.0: 10 port valve switches to INJECT. This injects the sample gas into the columns, after pressures have equalized.

Time 5.2: CH_4 elutes from column 1; 10 port valve switches to position LOAD; backflush through column 1 is on; CH_4 elutes through column 2.

Time 7.7: End of analysis; retention time for the methane peak was 4.0 min. and the total time of the process is 7.7 min.

SYSTEM PRECISION

The precision test consisted of repeated analyses of a gas sample (sample 1), with a methane concentration in air of 1723.7 ppbv, obtained from Randy Cofer, NASA Langley Research Center, USA. For groups of four injections, average peak areas (A) and standard deviations (s) were obtained. For a total of 19 groups, the hystogram of the relative standard deviations (s/A x 100%) is shown in Fig. 2. The overall average relative standard deviation is (0.47 ±

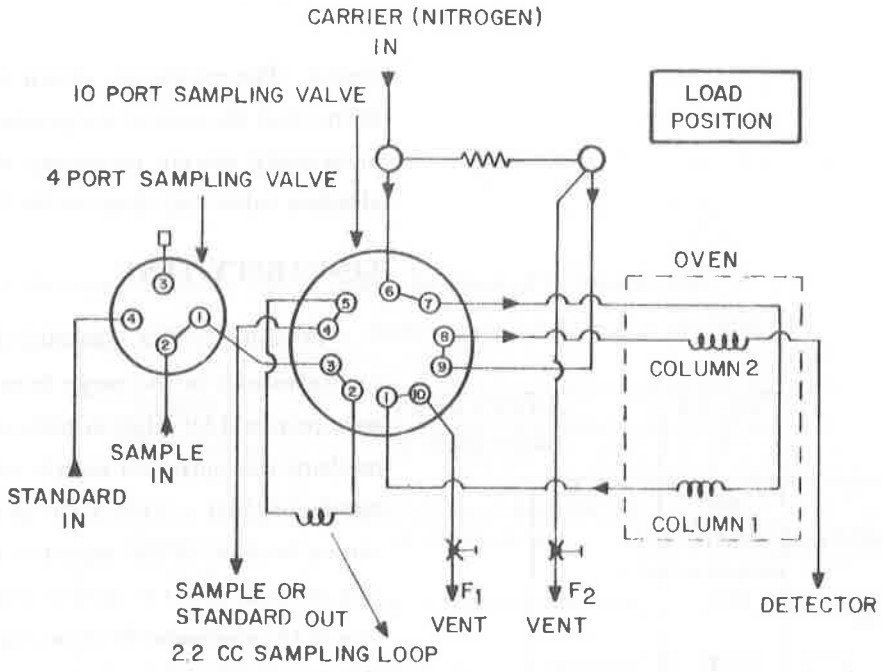

Figure 1. Gas chomatograph assembly for measuring methane. Gas sampling with back flush of column 1 to F_1 vent.

Sistema de cromatógrafo gasoso para medir metano. Amostragem de gás com retrofluxo da coluna 1 para F_1.

0.15)%. A second test using the same procedure was made with ambient air collected outside of the laboratory (sample 2). Again 4 injections were made for each group shown in Fig. 3, with a total of 11 groups. The average relative standard deviation for sample 2 was 0.41%.

Since one has to determine the average peak area of the calibration gas in order to determine the CH_4 concentration of an unknown sample gas, a net relative standard deviation of $(0.472 \pm 0.472)^{1/2} = 0.66$ results. Thus, the nominal maximum net standard deviation expected for the system is 0.66%. For typical concentrations of 1700 ppbv, this means a precision of about 11 ppbv.

REPRODUCTION TEST

Three air samples were collected at the same site (Massaguaçu beach, an Atlantic Ocean site, 200 km from São Paulo, Brazil) and almost at the same time (February 19, 1992, at 10:25, 10:27; 10:29). Two of these samples were analysed by our system and a third one was analysed at NASA Langley Research

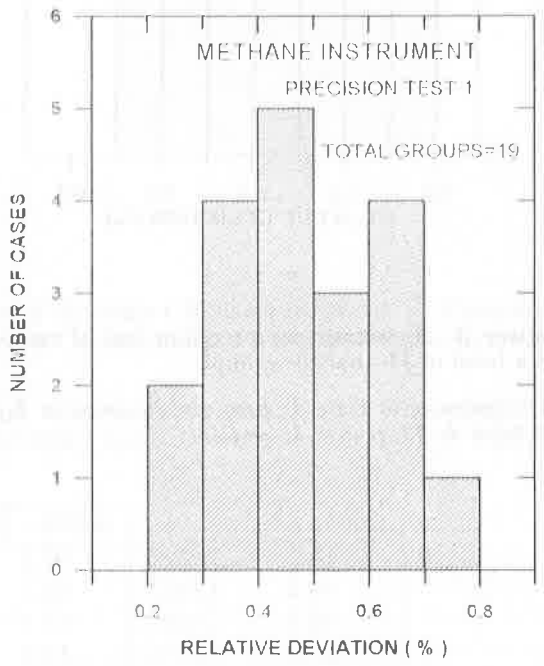

Figure 2. Histogram for precision test of sample 1 for a total of 19 analysis groups.

Histograma para teste de precisão da amostra 1 para um total de 19 grupos de análise.

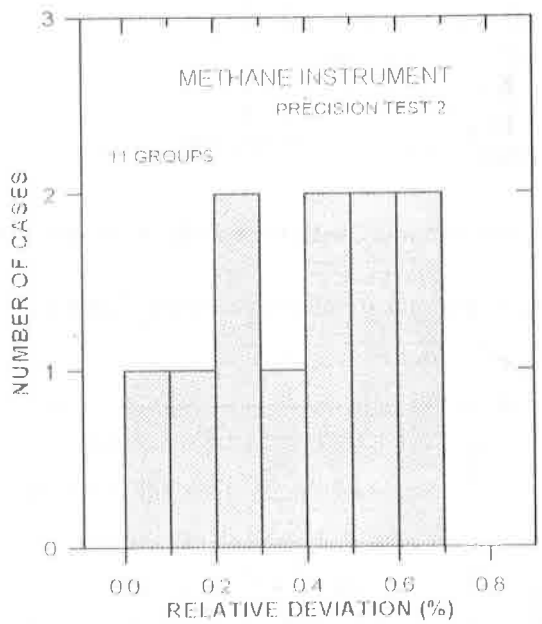

Figure 3. Histogram for precision test of sample 2 for a total of 11 analysis groups.

Histograma para teste de precisão da amostra 2 para um total de 11 grupos de análise.

Center. The results are shown in Table 1. They indicate that the system is reproducing well within the uncertainty margin previously shown and with the absolute value very close to the Langley value.

LINEARITY TEST

In order to test linearity, several known CH4 concentrations in the range from 1509 to 2515 ppbv were prepared by dilution with ambient air of a high methane concentration sample with nominal concentration of $(5.03 \pm 0.03) \times 10^4$ ppmv. This range was chosen because of the expected methane concentration in clean air. The system response for the injection of these samples is shown in Table 2. This table shows:

a) The system responses $\overline{y}$ (methane peak area) to injections of different samples with the same concentration have a relative standard deviation ranging from 0.0086% to 2.13% (column five). This can be explained by the method of sample preparation itself, where the precision of the measurement instruments implies relative deviations of 2%.

b) The difference between the system response $(\overline{y})$ and the corresponding value, determined by regression $\hat{y} = 4655 \pm 1.43x$ (last column), represents the system linearity response in this concentration range.

Fig. 4 shows the straight line obtained by regression analysis, as well as the 97.5% confidence intervals for it. These confidence intervals were obtained following Natrella (1963).

In Table 3 we show the maximum and minimum distances to the straight line for those values determined by the regression analysis considering 75% (fourth column) and 97.5% (last column) confidence intervals. These values suggest that there is 75% probability that our system response be linear in this concentration range, since the maximum relative distance to the straight line is about 3% (fourth column)

Table 1. Results of the reproducibility test in ppbv. Analysis of 20 March 1992.

Resultados do teste de reprodutibilidade em ppbv. Análise para 20 de março de 1992.

SAMPLE	PARAMETER	VALUE
Massaguaçu 10:25	# of injections	4
	Averages CH_4 concentration	1696
Massaguaçu 10:27	# of injections	4
	Average CH_4 concentration	1689
Massaguaçu NASA Langley Research Center	Average CH_4 concentration	1690

Table 2. System responses to injections of different samples with the same CH_4 concentrations, x. Comparison between the average of methane peak area measured values ($\overline{y}$) and those obtained using the regression line $\hat{y} = 4655 + 1{,}43x$.

Respostas do sistema para injeções de diferentes amostras com as mesmas concentrações x. Comparação entre as médias $\overline{y}$ de área de picos de metano e os valores obtidos com a linha de regressão $\hat{y} = 4655 + 1.43x$.

# of injections	x (ppbv)	$\overline{y}$	$s_{\overline{y}}$	$(s_{\overline{y}}/\overline{y} \cdot 100\%)$	$\hat{y}$	$((\overline{y}-\hat{y})/\overline{y}) \cdot 100\%$
3	1509	6659	73	1.10	6825	-2.49
3	1761	7446	144	1.93	7186	3.49
3	1861	7424	133	1.79	7329	1.28
3	2012	7366	157	2.13	7545	-2.43
2	2264	7905	35	0.44	7906	-0.013
2	2515	8258	0.71	0.0086	8266	-0.097

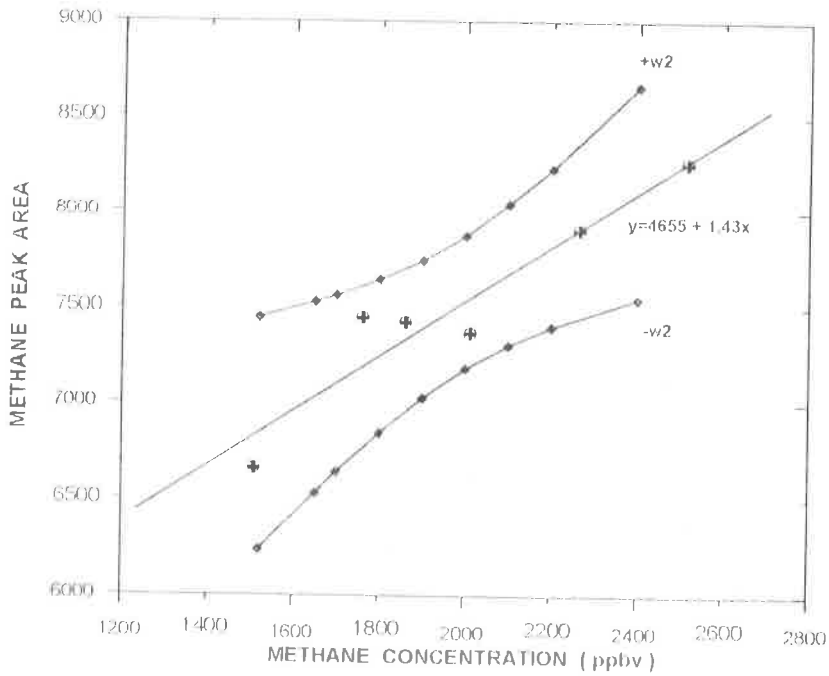

Figure 4. Regression line analysis of Table 3. The upper and lower limit curves show the domain of the 97.5% confidence interval.

Análise por linha de regressão da Tabela 3. As curvas limites superior e inferior mostram a região de 97,5% de intervalo de confiança.

and this value is compatible with the observed variability of our measured values. For the 97.5% confidence interval, the maximum relative distance to the straight line for those values calculated by regression analysis is two times larger than the observed variability.

In the range from 0.75 to 5 ppmv the dispersion is larger than for the previous range, as expected, but the correlation coefficient is still very close to unity, which gives confidence, when measuring sporadic contaminated samples with higher concentrations of CH_4.

SAMPLING RESULTS

Samples from different ecosystems and sites in Brazil have been analysed in preparation for the TRACE-A Brazil field mission (Kirchhoff et al., 1992) and the results are shown in Table 4. Average concentrations of methane are shown. All samples were collected about 0.5 m above surface. The values for Lontra and Campo Grande represent larger concentrations than those for the other sites. This preliminary tendency, which needs to be confirmed, may actually represent an expected result since these sites are near the Pantanal region, a natural large ecosystem flooded yearly during the wet season. Lowest values of CH_4 concentrations were observed at Natal, which always receives air masses from the ocean.

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Table 3. Maximum and minimum distances to the straight line for the values determined by regression analysis, considering 75% (w_1) and 97.5% (w_2) confidence intervals.

Distâncias máximas e mínimas relacionadas à reta determinada por análise de regressão considerando intervalos de confiança estatística de 75% (w_1) e 97,5% (w_2).

$\bar{x}$ (ppbv)	$\hat{y}$	w_1	$w_1.100\%/\hat{y}$	w_2	$w_2.100\%/\hat{y}$
1520	6841	261	± 3.82	605	± 8.84
1650	7027	216	± 3.07	499	± 7.10
1700	7099	200	± 2.32	462	± 6.51
1800	7242	173	± 2.39	402	± 5.55
1900	7385	156	± 2.11	360	± 4.87
2000	7528	151	± 2.01	347	± 4.61
2100	7671	159	± 2.07	370	± 4.82
2200	7814	179	± 2.29	416	± 5.32
2400	8101	242	± 2.99	559	± 6.90

$\hat{y}$ = Calculated value by regression analysis.

Table 4. Average methane concentrations from grab samples collected at different sites in Brazil, between January and April 1992.

Concentração média de metano de amostras coletadas em vários locais no Brasil entre janeiro e abril de 1992.

SITE	CH_4 CONCENTRATION (ppbv)	# OF SAMPLES
Cuiabá	1686 ± 8	5
Natal	1642 ± 11	2
Massaguaçu	1682 ± 32	5
Passo do Lontra	1985	1
Campo Grande	1741 ± 78	6
Goiânia	1681 ± 28	4

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