

Evaluation of a micro gas chromatographic technique for environmental analyses of CO₂ and C₁–C₆ alkanes

Giuseppe Etiope

ING-Istituto Nazionale di Geofisica, Via Vigna Murata 605, 00143 Rome, Italy

Received 7 January 1997; revised 14 March 1997; accepted 17 March 1997

Abstract

A performance evaluation of a portable gas chromatograph (Chrompack CP2002P), equipped with a micro thermal conductivity detection (micro-TCD) system was conducted for carbonious gases of environmental relevance, by analysis of calibration standards, atmospheric air samples and bottled mineral water samples compared with air-saturated water samples. The reliability of an headspace equilibration method has also been tested for application to gas dissolved in natural waters. The instrument has been tested for its sensitivity, reproducibility, linearity and retention time stability. The miniaturization technique of the micro gas chromatograph allows for analyses much faster than those of traditional TCD equipped gas chromatographs: complete run time, including C₆, is about 30 s. This rapidity may allow a large number of field data to be achieved over a short time and the immediate analysis on site may drive the survey strategy as the results are examined. © 1997 Elsevier Science B.V.

Keywords: Environmental analysis; Water analysis; Air analysis; Alkanes; Carbon dioxide

1. Introduction

Vadose zone and groundwater can be contaminated by a wide spectrum of noxious volatile substances, both natural and anthropogenic. Occurrence of light hydrocarbons in the ground may result from gas leakage from underground fuel tanks or methane pipelines. In special cases, C₁–C₆ gases may migrate upwards from deep seated oil fields, and their detection in the ground may be a useful tool for petroleum exploration. Significant amounts of carbon dioxide and methane, together with hydrogen sulfide and many volatile organic compounds (VOCs), may be released by landfills, affecting surrounding agricultural activity and groundwater quality. Carbon dioxide, resulting from biodegradation of organic compounds, has been found to be an effective

indicator of subsurface pollution by VOCs coming from landfills, industrial plants and organic solvent disposal sites [1]. The concentration of CO₂ and CH₄ in soil is an important determinant of the level of biological activity and a potential hazard when associated to gas emissions linked to volcanic, geothermal activity or any geological process involving gas accumulation and sudden release to the atmosphere. Moreover, the rates of CO₂ and CH₄ production in the ground and natural waters (groundwater and seawater), and the rate at which they are transferred to the atmosphere, have an important role in global C cycling.

So, the occurrence of gas in the shallow environments of the Earth may be object of study for several disciplines. In all cases the evaluation of degree and extent of contamination phenomena should be based

on sampling and analytical techniques which allow for acquisition of as many data points as possible; the comparison among several gaseous compounds, with different physicochemical behaviour, is also mandatory. Generally, economic factors limit the amount of sampling points and the number of gases to analyze. Conventional technologies available for subsurface investigation are based on quite slow and expensive sampling procedures, and therefore analyses are limited to few monitoring points; it does not allow either an exhaustive evaluation of the occurring contamination processes, or a study of their evolutive trends. Moreover, since prospecting data can be strongly biased, interpretation derived from a small data set could be even erroneous. In such a context, soil-gas surveying has become an effective field method to quickly assess the extent of subsurface pollution of gaseous and volatile compounds at highly reduced costs. The use of soil-gas sampling allows mapping of pollution plumes, defining its two-dimensional shape and location, and indicating groundwater contamination [2]. The integration of the soil-gas method and groundwater analysis, with the use of a portable detector for rapid on-site analyses, should offer a better ratio between data quantity (in terms of number of samples and number of gaseous species for each sample) and costs.

In the present paper results of an evaluation of a fast, portable micro gas chromatograph are presented for CO_2 and light hydrocarbons (C_1 – C_6), through multiple analyses of calibration standards; CO_2 and CH_4 have been also measured in atmospheric air samples, bottled mineral water samples (with known CO_2 concentration) and air-saturated water samples. Air-saturated water is the theoretical dissolved gas concentration based on the assumption that the atmosphere is the sole source of the gas in question and that air–water equilibrium conditions prevail. The air-saturated water level can be calculated by multiplying the atmospheric partial pressure of the gas by the appropriate solubility coefficient. Basically, atmospheric air and air-saturated water for CO_2 and CH_4 represent natural reference levels for soil-gas and natural water analyses, respectively. The quality control of the GC response for such backgrounds is essential for field surveys.

2. Experimental

2.1. Apparatus

Gas analyses have been performed by a portable micro gas chromatograph Chrompack, Model CP2002P, based on silicon micromachined technology (Ref. [3] and references therein). It contains two independent miniature GC modules. Each module is equipped with a sample injection system, an analytical column with oven and a micromachined thermal conductivity detection (micro-TCD) system. The sample injector is miniaturised with a volume of the sample chamber of only 8 μl . The gas sample is sucked by a small vacuum pump and its quantity is controlled by an opening time valve, which can be set from 0 to 255 ms. Generally, about 200 nl of gas is introduced in 255 ms. A single injection is required as the sample is then separated into the two columns. The total dead volumes are less than 2 nl and this leads to a noteworthy increase in sensitivity of the micro-TCD, much higher than traditional TCD methods.

The instrument tested for the present study has been configured to analyse carbonious gases of environmental relevance, such as CO_2 and C_1 – C_6 alkanes (methane, ethane, propane, butane, pentane, hexane). The first module mounted a Hayesep A column (25 cm \times 0.5 mm) micro-packed with porous polymers. This column can separate N_2 + O_2 , CO_2 , CH_4 , C_2H_6 , H_2S , SO_2 . The second module mounted a CP-Sil 5 CB (4 m \times 0.15 mm), which can separate hydrocarbons and a wide number of VOCs. Helium was used as carrier gas from a built-in gas cylinder. An integrating software (MAESTRO II, Chrompack, Netherlands), in a portable PC486, is used for remote-control of the gas chromatograph, integration of peaks, elaboration and charting of the analytical results.

2.2. Procedure

The micro-GC has been tested for analysis of carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}) and hexane (C_6H_{14}) by using calibration

standards (Scotty, Alltech, Italy); CO₂ and CH₄ have been also measured in atmospheric air samples, bottled mineral water samples (in which CO₂ concentration is reported to be 5 mg/l) and air-saturated distilled water samples. Calibration standards were prepared by dilution to obtain CO₂ and CH₄ four-point curves covering atmospheric air and air-saturated water levels [CO₂: 1%, 1000 ppmv, 350 ppmv, 100 ppmv; CH₄: 1%, 100 ppmv, 15 ppmv, 1 ppmv]. C₂–C₆ standards were at few ppmv levels, as may occur in certain contaminated grounds (15 ppmv, 7.5 ppmv, 1.9 ppmv, 0.5 ppmv).

After calibration, 5 sets of ten analyses of 350 ppmv CO₂ and 15 ppmv C₁–C₆ standards were performed in five different days, with time gap up to 1 week, to check reproducibility and retention time stability. Standard samples were injected by a 5 ml plastic syringe into a capillary equipped with filters and connected to the micro-GC injection port.

Fifty atmospheric air samples (collected far from urbanised areas) were analysed in duplicate over five days (ten samples per day). Atmospheric air was sucked directly by the micro-GC through the capillary connected to the injection port.

Mineral water samples were obtained from a single bottle, commercially available, whose CO₂ content is reported to be 5 mg/l. Air-saturated water was prepared by equilibrating distilled water with atmosphere in open vessels at controlled temperature (20°C). All water samples were analysed by headspace equilibration method [4,5]. Over three days ten 6 ml mineral water samples and thirty 6 ml air-saturated water samples were inserted in 12 ml septum vials. Samples were, then, agitated and left standing at ambient temperature, 20°C, for at least 15 min before analysing. In order to avoid variability in the manual operation with syringes, the capillary connected to the micro-GC injection port was inserted directly in the headspace vials through the rubber septum. Each headspace analysis has been performed in duplicate and bracketed by a sample of atmospheric air.

By knowing the gas concentration in the headspace vial (C_G), the Bunsen solubility coefficient (β), the gas concentration in atmospheric air (C_{AA}) and the volumes of the liquid and headspace (V_L and V_G), the initial gas concentration in water (C_L^0)

before equilibrium can then be determined according to the equation:

$$C_L^0 = (C_G - \beta) + (C_G - C_{AA}) \frac{V_G}{V_L}$$

For air-saturated water samples, this means that the gas concentration in the headspace vial must result equal to the concentration in atmospheric air, irrespective of the gas–water volume ratio. Theoretically the error in C_L^0 increases as the concentration of gas in the original water sample departs from the equilibrium concentration with respect to atmospheric air. The main sources of error include the precision in the measurement of V_G and V_L , the Bunsen coefficient variability as a function of the water temperature and salinity and the analytical error.

3. Results and discussion

3.1. Calibration standards

The chromatograms of the standards showed that the area under each gas peak was proportional to the gas concentration but it was largely dependent upon the integration method adopted. Thus, calibration standards have been preliminarily used to find the best GC method (instrument working parameters and integration parameters) of analysis. The Hayesep A 40°C column temperature, 113 kPa column head pressure and the CP-Sil 5 CB 50°C temperature and 125 kPa column head pressure provided the best peak splitting and resolution for the gases under study. Accordingly, on the Hayesep A column, the methane peak started to emerge about 6 s after injection, the CO₂ peak emerged at 17 s and the C₂H₆ peak at 30 s. C₃–C₆ peaks on the CP-Sil 5 CB column were at 8, 9.1, 14.6 and 27.4 s, respectively. Figs. 1 and 2 show typical recorder traces for some standards. Some coelution problems may rise for those peaks eluting at lower retention times (methane, propane and butane), close to air peak (in the Hayesep A column) and air and water peaks (in the CP-Sil 5 CB column). In these cases peak splitting and accurate integration events are needed.

To evaluate the concentration range for C-gases,

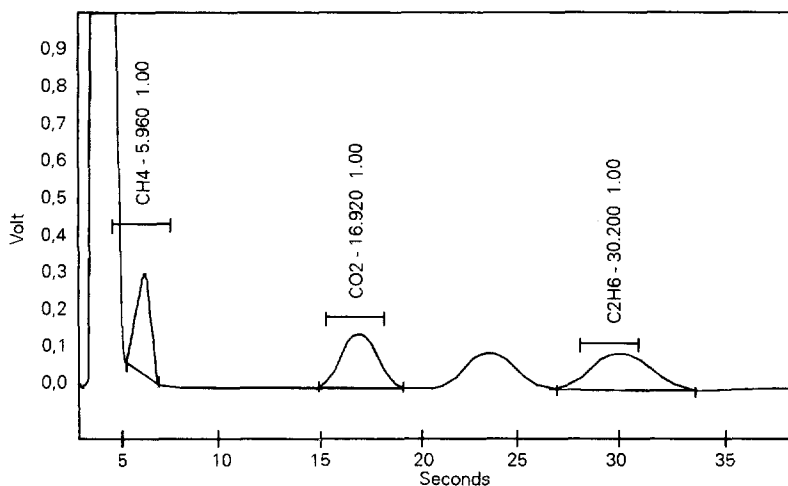


Fig. 1. Chromatogram of 1% methane, carbon dioxide, ethane standards (Hayesep A column). The first and fourth peak refer to nitrogen (balance gas) and 1% ethylene, respectively, not considered in the present work.

over which the micro-GC can be used, the limit of quantification (LOQ) has been calculated. According to IUPAC [6], LOQ, is defined as a signal that is 2 times the noise. It has been derived by using experimental data provided by Chrompack and considering the retention time for each gas. Table 1, column 2, lists the LOQ of the gas analysed. Analysis of standards, however, suggested that a sensitivity of 0.5 ppmv may be easily got for CH_4 and C_4H_{10} .

The reproducibility in instrumental response is indicated by relative standard deviation (Table 1, column 3). Considering a period of five days during which the instrument is daily turned on and off, reproducibility resulted to range from 3.8% for CO_2 , to 21% for ethane. Gases eluting at higher retention times show lower reproducibility.

The instrument linear response has been determined by four-points calibration curve (forced to zero) and expressed in terms of coefficient of de-

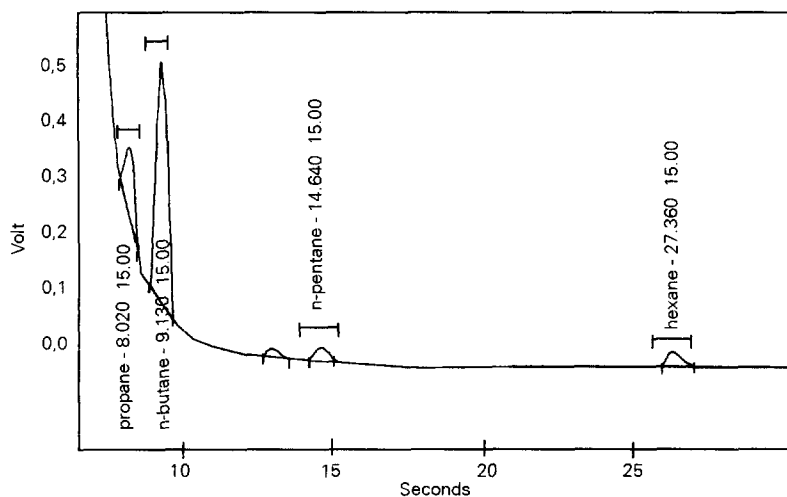


Fig. 2. Chromatogram of 15 ppmv propane, butane, pentane and hexane (CP-Sil 5 column).

Table 1

Limit of quantification (LOQ), reproducibility, linearity and retention time stability (R.T.S.) over five days during which the instrument is daily turned on and off

Gas	LOQ (ppmv)	Reproducibility (R.S.D., %)	Linearity (r^2)	R.T.S. (R.S.D., %)
<i>Hayesep A column</i>				
Carbon dioxide	7	3.8	0.998	0.5
Methane	2.4	9.6	0.991	0.9
Ethane	2.2	21.0	0.980	1.2
<i>CP-Sil 5 CB column</i>				
Propane	0.5	12.6	0.989	0.6
<i>n</i> -Butane	0.7	8.4	0.992	0.9
<i>n</i> -Pentane	1	14.3	0.983	0.7
Hexane	2	10.4	0.979	1.11

termination r^2 (Table 1, column 4). It was between 0.979 for hexane and 0.998 for CO₂.

The retention time stability, in terms of percentage standard deviation, is shown in Table 1, column 5. The knowledge of variations in the retention times is useful because the integration method identifies gases within a prescribed percentage window of the standard chromatograms. All gases showed a good retention time stability, although integration parameters, such as baseline or peak start/stop, have to be slightly modified as gas concentrations changes (increases or decreases) in comparison with standards. The retention time stability generally decreases as the retention time increases.

3.2. Atmospheric air samples

Fig. 3 shows a typical recorder trace for atmospheric air. CO₂ and CH₄ concentration in fifty samples averaged 366 ppmv and 1.53 ppmv, respectively, consistently to the atmospheric standard values. Table 2 lists the main descriptive statistics of

Table 2
Main statistics of atmospheric air analyses (ppmv)

Gas	Mean	Min.	Max.	R.S.D. (%)	<i>n</i>
CO ₂	356	350	406	4.3	50
CH ₄	1.53	1.1	2	17.6	50

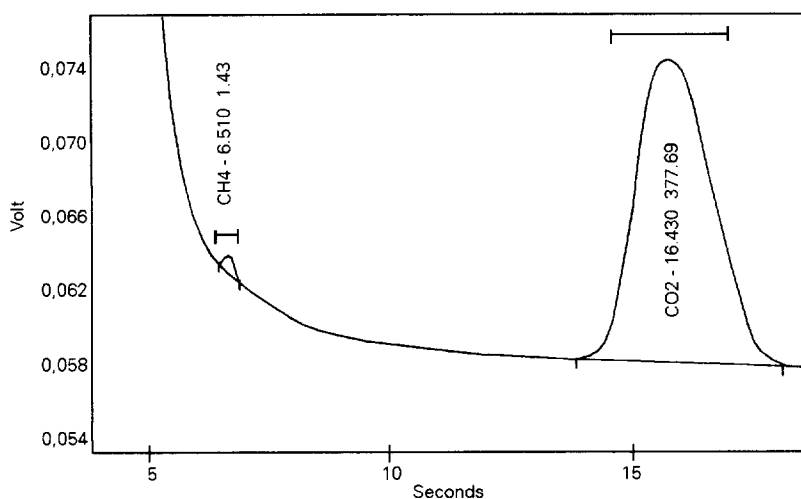


Fig. 3. Typical micro-GC chromatogram of atmospheric air (Hayesep A column). The first large peak refers to nitrogen + oxygen, not considered in the present work.

Table 3
Main statistics of CO₂ and CH₄ in mineral water samples (μg/l)

	Reported value	Mean	Min.	Max.	R.S.D. (%)	<i>n</i>
CO ₂	5000	3800	3100	4350	10.2	10
CH ₄	–	0.0280	0.0158	0.0420	25	10

such analyses. Analyses are performed over 5 days (ten analyses per day) and no significant variations were recorded in the GC response during this period.

3.3. Water samples

Table 3 lists the main CO₂ and CH₄ descriptive statistics of mineral water and air-saturated water analyses, referring directly to the gas concentration in water (μg/l), based on the solubility coefficients at 20°C [7] the measured atmospheric air concentration and the gas/water volume ratio (=1) in the vial. The CO₂ concentration in mineral water is comparable to the 5 mg/l value reported by the manufacturer. It should be considered that the manufacturer analysis refers to water at the spring and some degassing from the bottles is expected over time; thus the lower mean value of 3.8 mg/l is coherent. However the most important factor is the good repeatability of the values, in terms of relative standard deviation computed over three different days. The mean CO₂ content of air-saturated water samples is 0.59 mg/l, consistent with the theoretical level at 20°C (Table 4).

The relative standard deviation of water analyses is higher than that in the calibration standards and atmospheric air analyses; this is due to higher variability and bias potential in water analysis, related to several factors such as preparation and manual operation of vial samples including, eventually, incomplete equilibrium between air and water. Thus an important factor influencing its precision is the operator.

Table 4
Main statistics of CO₂ and CH₄ in air-saturated water samples (μg/l)

	Theoretical air-saturated water (20°C)	Mean	Min.	Max.	R.S.D. (%)	<i>n</i>
CO ₂	562	593	510	741	11.1	30
CH ₄	0.0264	0.0264	0.0132	0.0396	31	30

4. Conclusion

The most important characteristic of the micro-GC is the stability in retention time and repeatability, even over long periods during which the instrument is daily turned on and off. This property is rarely provided by traditional desk gas chromatographs. Peak splitting and accurate integration events are needed for those peaks (methane, propane and butane) eluting at lower retention times, close to air and water peaks.

The integration of micro-GC with the headspace equilibrium method provides an effective way for analysis of gas dissolved in water, easier and faster than other techniques (see Ref. [4]). Certainly this methodology is not affected by errors typically occurring when gas is stored into bias-bearing samplers and transported to the remote laboratory for analyses. Above all its rapidity allows for acquisition of a wide number of data over few time, with the possibility of statistical evaluations; moreover, the immediate analysis on site may drive the survey strategy as the results are examined, e.g., replicating sampling and analysis in case of unclear data or suspected anomalies, or changing sampling coordinates: this is very important for a correct and exhaustive environmental and geochemical characterisation of the ground and natural waters.

Acknowledgments

Thanks are due to G. Stani (Chrompack Italia) and

G. Barone (Ascotec S.r.l.) for assistance and technical support.

References

- [1] K.H. Suchomel, D.K. Kreamer, A. Long, *Environ. Sci. Technol.* 24 (1990) 1824.
- [2] H.B. Kerfoot, *Environ. Sci. Technol.* 21 (1987) 1022.
- [3] R.C.M. de Nijs, J. van Dalen, A.L.C. Smit, E.M. van Loo, *J. High Resolut. Chromatogr.* 16 (1993) 379.
- [4] C. McAuliffe, *Chem. Geol.* 4 (1969) 225.
- [5] J.-I. Ishibashi, I. Wakita, Y. Nojiri, D. Grimaud, P. Jean-Baptiste, T. Gamo, J.-M. Auzende, T. Urabe, *Earth Plan. Sci. Lett.* 128 (1994) 183.
- [6] G.L. Long, J.D. Winetordner, *Anal. Chem.* 66 (1983) 712A.
- [7] W.S. Broecker, T.H. Peng, *Tellus* 26 (1974) 1.