

CONDUCTING SOIL GAS SURVEYS OF NEW ZEALAND GEOTHERMAL AREAS WITH A PORTABLE MASS SPECTROMETER

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SUMMARY - An investigation into the feasibility of conducting soil gas surveys with a portable quadrupole mass spectrometer connected directly to the sample hole. The study site in the Tauhara Geothermal Field covered hot and cold ground along a 120m line. The results are presented in a semi-quantitative format as bar graphs for CO₂, H₂S, CH₄, He and Ar plus two unusual gases for geothermal areas, COS and C₂H₆. The suitability of the mass analyser for this type of field work are discussed along with its wide dynamic range and multi-gas detection capability. Also discussed is how the method can illustrate the difference between conductively and convectively heated ground. A suggested future application, searching for buried faults in geothermal areas, is discussed briefly.

1. INTRODUCTION

Understanding a complex system from a chemical perspective usually involves the collection of samples for the analysis of one or more of the components that make-up the system. When the system is accessible, obtaining the required samples is usually a straight-forward procedure. For geological systems, such as buried ore bodies and oil, gas or geothermal reservoirs, direct sample collection is not possible. A drill hole into the system can provide the necessary samples, but at a considerable cost that increases in proportion to the depth of the system. It is therefore more cost effective to conduct preliminary studies at the surface using indirect means, such as the geophysical methods developed for geothermal areas (i.e., resistivity measurements, heat flow studies and magnetic and gravity surveys).

Indirect chemical methods for the preliminary assessment of a geothermal system have required the presence of surface features, such as fumaroles and hot springs, to provide water and steam samples for chemical analysis. Soil gas surveys are a relatively new technique that offer a means of collecting geothermal chemical data when there are no surface emanations or wells, and can provide supplementary data when surface features are present. The method is based on the detection of concentration anomalies in gases or volatiles collected at the surface over a suspected ore body or energy resource. One or more gases that can be related to the deeper system (eg., reactions between ore bodies and the surrounding rock environment or degassing due to boiling in a geothermal reservoir) are chosen for the survey. Soil gas techniques, developed in the 70's and 80's for mineral exploration (McCarthy & Reimer, 1986 review), have been applied with some success to the study of geothermal systems over a number of years in several countries, including New Zealand. Some surveys have concentrated on a single species, such as Hg vapour (Noda,

1981) or radon (Whitehead, 1984), but most look at several species (Hg, CO₂ and Rn, Koga, et al., 1982; Hg and CO₂, Sheppard, et al., 1988; He, H₂, CO₂, CH₄ and Rn, Bertrami, et al., 1990; He, CO₂, O₂, and N₂, Hinkle, 1991; CO₂, H₂S, CH₄, "air" and H₂O vapour, Finlayson, 1992b). A similar technique called "geogas", looks not at gases migrating from a deep system, but at the ultra-trace quantities of particulates carried to the surface by these gases, and provides an indication of the relative quantities of heavy metals, and such non-metals as Si, S, Cl and As, present at depth (Christenson, et al., 1988).

The sampling of soil gases may employ direct collection or static collection, usually at depths of one half to one metre, by one of several techniques which are used separately or in combination. Collecting samples at one metre has the advantage of excluding most of the meteorological effects that influence more shallow samples. Static sampling employs a gas-specific absorbent placed in the ground for a period of time before it is returned to the laboratory for analysis. Examples of absorbents that have been used in geothermal soil gas studies include molecular sieves for CS₂ and COS (Hinkle and Harms, 1978), gold wire for Hg (Noda, 1981), and activated charcoal for hydrocarbon gases (Klusman and Voorhees, 1983, Noda, et al., 1992). Radon may be analysed on site at the time of collection (Noda, et al., 1982; Baubron, et al., 1991) or detected by means of a film absorber left in the ground, which is preferred by some investigators as it provides an integrated signal (Whitehead, 1984). Soil itself acts as natural gas absorbent and may be collected and analysed for absorbed gases or volatiles. Mercury surveys are often based on this method (Koga, et al., 1982; Prijanto, 1986; Sheppard, et al., 1990) and Nicholson, et al. (1989) reported on the use of soil-absorbed NH₃ as an exploration tool for low-enthalpy geothermal systems.

The third **soil gas** technique, direct collection, in which gas is extracted **from** the pore space of soil by pumping, **requires** a sealed hole, preferably one **half** to one metre deep. The hole can **be drilled** by hand and **fitted** with a pipe or hollow sampling probe which is **sealed** around its outer circumference. Alternatively, a steel **probe** can be driven into the ground with a sledge hammer, although it can be difficult in some **soils** to reach a depth of one metre and even more difficult to remove the **probe**. The direct method is **better** suited for **gases** that **are** non-condensable at ambient temperature and pressure (He, **Ar**, CO₂, CH₄, H₂S, etc.) rather **than** for volatile constituents such as Hg. Analysis can be done on site or the gas **can** be collected in evacuated containers for later, laboratory analysis. Direct collection into evacuated containers for **laboratory** analysis of CO₂, CH₄, H₂, and He was used by Bertrami, et al. (1990) in a study of several **Italian** geothermal **areas**, and Hinkle (1991) used **similar** techniques to monitor He, CO₂, O, and N₂ in **soil** gases from the Roosevelt Springs geothermal field in the **U.S.A.**

While **laboratory** analysis **has** several advantages (eg., concentration of field time on sample collection; the convenience of **a** more stable environment; **access** to larger, more sensitive analysers), field analysis allows **better** management of the **soil** gas survey. It is a **major** advantage, for example, **to** know **that** a sample **from** a particular site is "good" (e.g. consecutive runs give the same analysis); if not it **can** easily be repeated under the same sampling and weather conditions.

A number of analytical instruments have been **used** for field analysis of **soil** gases in geothermal and volcanic **areas**, including scintillation counters for Rn (Koga, et al., 1982; Baubron, et al., 1991), infra-red spectrometers for CO, (Sheppard, et al., 1990; Baubron, **et** al., 1991), gas chromatographs for inorganic gases and simple hydrocarbon gases (Sheppard, et al., 1990; Finlayson, 1992b), leak detector mass spectrometer for **He** (Baubron, et al., 1991), and quadrupole mass spectrometers for all **gases** and vapours with a **mass** of 100 or less (Baubron, et al., 1991). Each method **has** advantages depending on the application, such **as** sensitivity and specificity (scintillation **counters**; He leak detectors) or multi-gas detection per sample (**gas** chromatography; **mass** spectrometry).

This paper describes **an** investigation **into** the feasibility of using **a** portable quadrupole **mass** spectrometer for direct on site analysis of **soil** gases in geothermal **areas**. The unique feature of **this** study is the direct connection of the mass analyser to the **sampling** probe, whereby **the** interstitial **soil** gases **are** pumped directly to the inlet of the mass spectrometer, using only an ice-water cooled trap to reduce the amount of water vapour reaching the instrument (especially necessary when holes drilled in the hottest ground became **steam** fumaroles !).

2. STUDY AREA

The site selected for this work lies within the Tauhara

Geothermal Field, which is situated along the north-eastern border of the **town** of Taupo in the centre of the Taupo Volcanic Zone of **New** Zealand's **North** Island (Figure 1). The **regional** and surficial geology and the local hydrology of Taupo and the Tauhara field have been summarised by Henley and Stewart (1983). The important features **for** this study **are** the highly permeable **and** porous pumice breccias that make up the surface layers in **this** region and overlie the high permeability Wairakei Lapilli Tuff Group. This latter formation is believed to contain the shallow hot water aquifer (at a depth of approx. 70m) tapped by most of Taupo's domestic hot water wells. The survey **area**, part of a paddock for sheep and cattle, is directly east of the back fence of the Taupo Golf Club's Centennial course and approximately 200 metres **SW** of TH1, one of the deep exploration wells drilled in the Tauhara field in the mid-1960's. It was chosen for **ease** of access, close proximity to the Wairakei Research Centre (13km) and **because** the site was used by geophysicist **colleagues** for a ground temperature survey from 1989 to 1991 (Mongillo, pers. communication, 1992). In that study, ground temperatures were measured **from** the **surface** to a depth of one metre along a line running in an east-NE direction from the golf course fence for approximately **120** metres. The temperature transect **started** in "cold", grass-covered ground, and proceeded through gradually increasing **soil** temperatures towards a patch of hot, faintly steaming ground, **bare** of any vegetation. We believed that **a** **soil** gas survey line parallel to the temperature transect and encompassing the same temperature extremes would provide an excellent test of the gas probe-mass spectrometer system. For **our** purposes, we **selected** a spacing of 10-metres between sampling holes, starting **the** first hole (TH-1) approximately 10 metres **from** the golf course boundary and **proceeded** east-NE to the final hole (TH-12) just past the furthest boundary of the hot patch of ground (Figure 1).

3. EXPERIMENTAL

Gas samples were collected from a 1 metre deep hole which had been drilled with a hand auger. A **probe** was **inserted** into the holes and pumped to remove atmospheric **gases** before connecting it to **the** mass spectrometer **via** tubing and an ice-water cooled water vapour **trap**. The design and operation of **the** **probe**, which was built for an earlier **soil** gas survey, is described by Finlayson, 1992a). The temperatures **at** the bottom of each hole (downhole temperature) and at the surface (**air** temperature at ground level) were **measured** with a 1.5m **K-type** (chromel/alumel) probe and a Fluke **52 Series** digital thermometer. Atmospheric pressure was not recorded because the survey (with the exception of the first hole, TH-1/92) was completed in one day. TH-1/92 was drilled on the previous day, but further work on that day was not possible **as** the hand auger broke while **drilling** that hole.

The mass analysing system used for **this** study **was** designed and assembled by one of the authors (J. Patterson) and was also **operated** by him during the field work. The mass spectrometer was a Dycor Quadrupole **Gas** Analyzer, Model

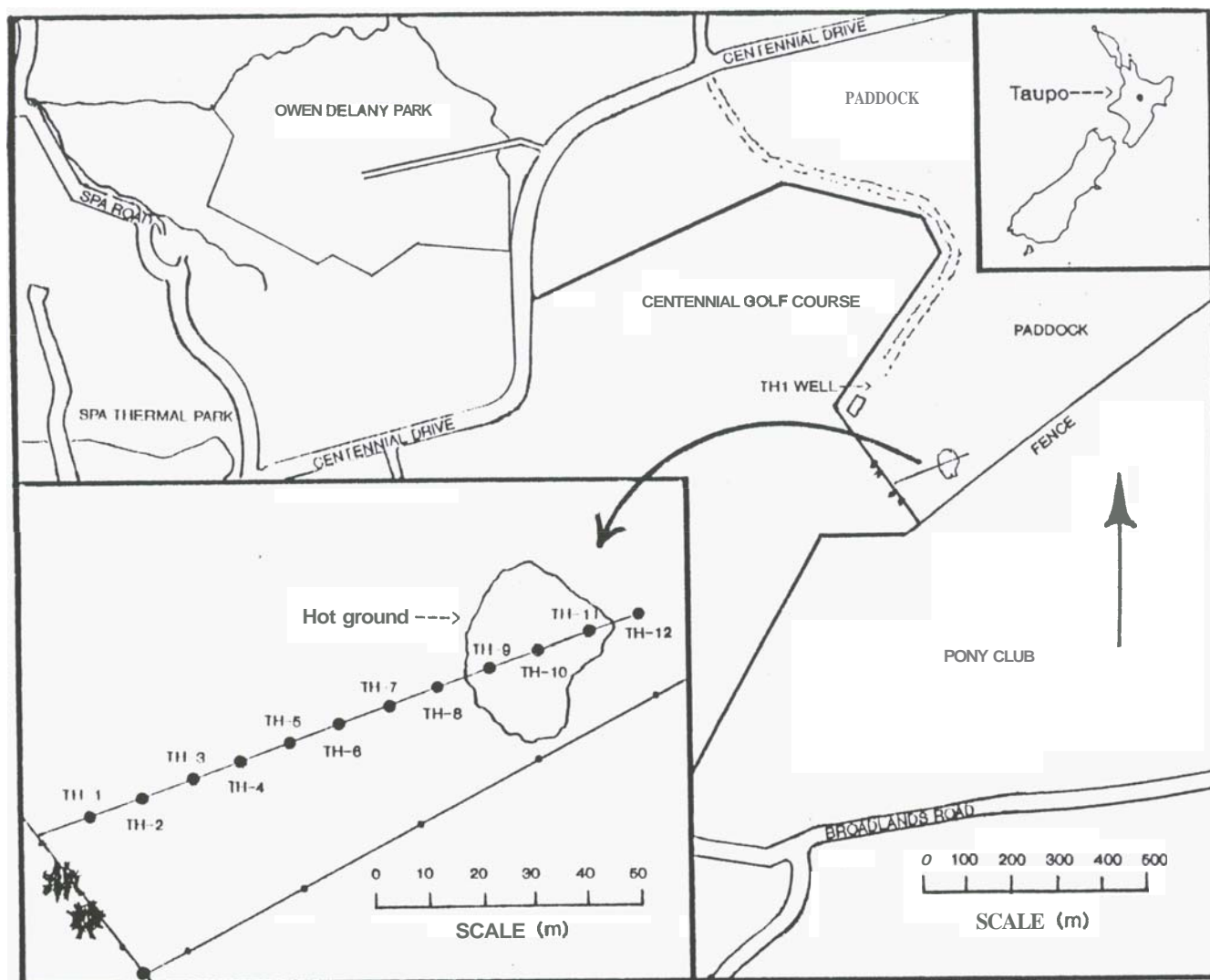


Figure I- Location map of Tauhara soil gas survey line with sample sites indicated

MA100M with a nominal mass range from 1 to 100 daltons (actual range was 1 to 150 daltons). After an initial, rough pump down in the laboratory, the working vacuum was maintained while travelling and in the field by a Varian 30 litre/second triode Vacion pump. Two power supplies were used to operate this ion pump, a small 6 kV supply for travelling and a more powerful high voltage supply for the field work. Four, linked Portalac 40 amp-hour lead acid batteries supplied the electrical current to run the pump supplies and the mass spectrometer via an Ebbet Automation 12 volt DC to 220 volt AC inverter. The batteries were capable of powering the system for approximately 8 hours of field work before requiring an overnight recharge.

The sample train from the sample probe to the mass spectrometer is shown in Figure 2. Filtering was provided by an ice-water cooled trap for water vapour and by a Nupro 0.5 micron filter to protect the inlet valves and membrane. The inlet to the mass spectrometer consisted of a silicone membrane backed by a stainless steel frit. The middle arm of a stainless steel tee was attached to the membrane inlet so that sample gas could be flowed past the inlet by means of a small battery-powered pump. Two

stainless steel valves were used to isolate the membrane inlet from the sampling train. The sampling pump was operated with a speed controller so the sample train could be flushed-out quickly and then, with the mass spectrometer inlet open, pumped for sampling at a low speed (approx. 100 ml/min).

The mass spectrometer was operated by a laptop computer (Toshiba 1200) using MASSPORT software developed by Patterson. In addition to turning the instrument on and off, the computer was used to start a run by scanning through a mass range entered into the computer (usually 1 to 100 daltons). After about 30 to 40 seconds, the results would be displayed on the computer screen as a mass spectrum of the gases from the hole being sampled. Two runs were made at each site and, in the majority of cases, produced identical mass spectra. Occasionally additional runs were required before successive runs produced identical spectra and the probe-analyser system could be moved to the next hole. The computer also contained software to convert the mass spectrum data for a particular gas species (or mass number) into a bar graph or other suitable format for each hole sampled up to that point.

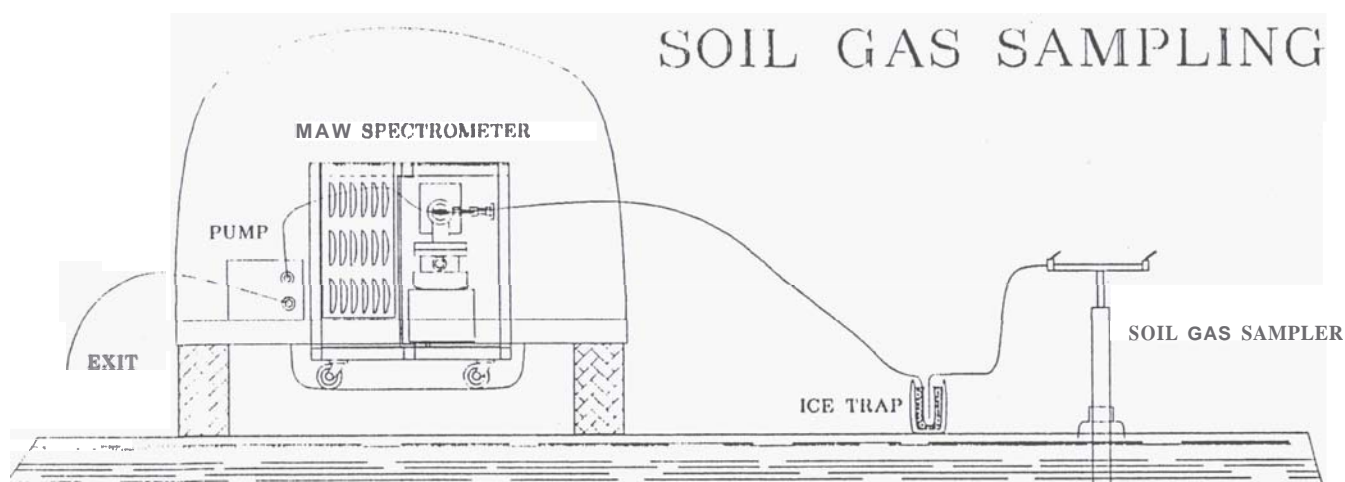


Figure 2. Schematic diagram of sample probe and vehicle-mounted quadrupole mass spectrometer

For transportation and use in the field, the mass spectrometer was secured in the rear of a station wagon with a cargo strap and the batteries were stored in two wooden boxes that fitted on the floor behind the passenger seat. The large ion pump power supply was mounted in a third wooden case and secured next to the spectrometer. Other smaller items such as tubing, cables, tools and test instruments were stored in a fourth box.

4. RESULTS

Because our purpose was to determine the feasibility of soil gas analysis at the point of collection, we did not calibrate the mass spectrometer and reduce our data to quantitative values. It was sufficient to present the data in a way that would portray the relative changes in gas levels for a particular species between each sample point along the survey line. Figure 3 shows the results as bar graphs, where the height of the bar represents the partial pressure of that particular species in the mass spectrometer and the points on the x-axis are the numbers of the sample holes. For clarity, the "TH-" designation of the sample hole numbers was not used in these plots. In most cases, additional bars have been plotted which represent lighter ion fragments split from the principal mass of a particular gas (eg., 28 m/z, CO^+ ; 16 m/z, O^+ ; and 12 m/z, C^+ from 44 m/z, CO_2). The gases plotted in Figure 3 are the usual gases associated with geothermal systems in New Zealand (CO_2 , H_2S , CH_4 , He, and Ar) plus some unusual species that appeared to be present at some sites, although at very low levels (carbonyl sulphide, COS and benzene, C_6H_6). Hole number 2 does not appear on the graphs because it was never drilled owing to failing daylight and a lack of time to return the following day to complete it.

The downhole temperature at each site has been plotted as a line graph on each of the bar graph plots in Figure 3 so that correlations between temperature and gas levels are more apparent. Air temperature at ground level was also measured at or nearby each site and these temperatures reflect the time of day more than anything else, with a low of 11°C in the morning and a high of 16°C in the late

afternoon. Table 1 shows the analyses in mole % of three duplicate gas samples taken from TH-9 at a later date and analysed by gas chromatography and titrimetry in the laboratory. These results are provided to give the reader an indication of the actual concentration of the conventional gases present in the soil gases from the patch of hot ground (TH-9, -10, and -11).

5. DISCUSSION

5.1 Mass Spectrometer Performance

The mass spectrometer used in this investigation was originally set up in a laboratory environment to monitor, among other things, hydrocarbon gases generated by catalysis studies. Although it was necessary to convert the instrument to a portable, battery-operated mode for the soil gas work, the necessary equipment and design for this were already in place. The resulting portable system, however, had not been field tested and had not travelled more than a few kilometres from its home base near Wellington. It easily passed the first test of this study, a 400 km highway drive to Wairakei and a short, but very bumpy drive across a paddock to the field site with no apparent effect on the operation of the mass spectrometer. It was also apparent at the end of this study, that the four 40 amp-hour 12 volt batteries were sufficient to operate the analyser system for a reasonable period in the field (approximately 8 hours), providing that access to an AC power line was available shortly afterward for an overnight recharge of the batteries.

Of greater concern was the effect the sample gases might have on the mass spectrometer, especially with regard to its operation and to corrosion. Before going to the field site, the system was tested on the lawn outside the Wairakei laboratory. In this trial the ice-water trap was not used and it is believed that this resulted in water vapour entering the inlet. This was believed to be the cause of the ion pump shutting down with the near loss of the working vacuum. The vacuum was recovered and the ice trap was made a permanent fixture of the sample train. No obvious evidence of corrosion was found at the conclusion of this work, but

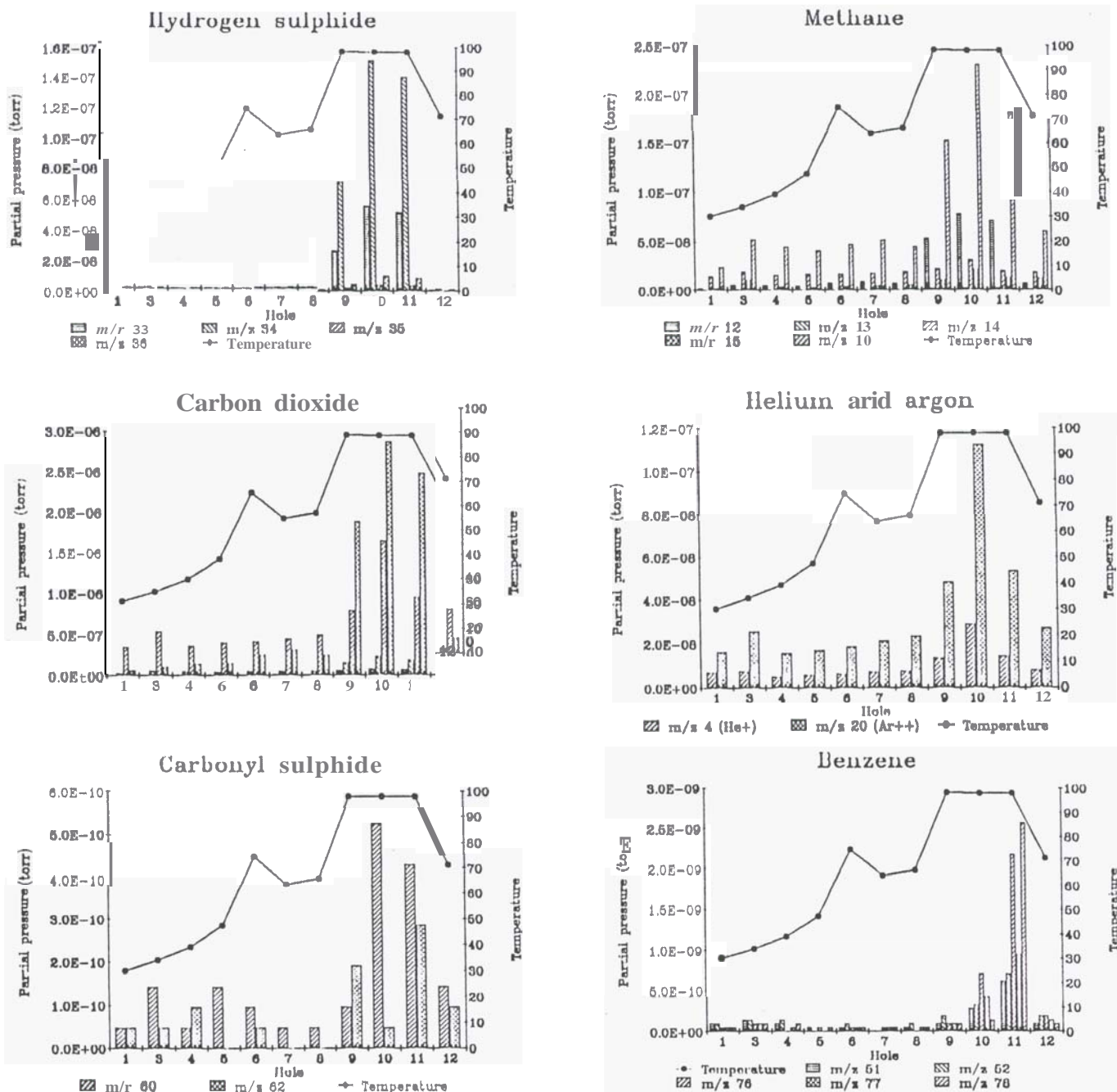


Figure 3-

Bar graph plots for six soil gases measured on the Tauhara survey line. The downhole temperatures line graph has been plotted on each bar graph.

Table 1- Analysis of three gas samples from TH-9

Gas	Mole %			
	7010-2-N	7010-3-N	7010-4-N	Average
CO ₂	92.6	92.9	92.8	92.8
H ₂ S	3.98	3.81	3.80	3.86
He	0.00040	0.00026	0.00023	0.00030
H ₂	0.60	0.62	0.60	0.61
O ₂	0.0091	0.0093	0.033	0.017
N ₂	1.31	1.17	1.29	1.26
CH ₄	1.47	1.50	1.42	1.46
Ar	0.011	0.0092	0.011	0.010
Total	99.98	100.01	99.95	100.02

there were signs of some very minor corrosion products in the inlet system when this equipment was later used for a more extensive survey in the Rotorua geothermal field. Overall, the mass analyser system operated very well, with no serious problems, even when the three 98°C holes (TH-9, -10, and -11) were sampled. These three holes became steam fumaroles as soon as the hand auger was removed from the hole, which required careful monitoring of the ice-water trap to add more ice to prevent water vapour overload.

5.2 Tauhara Survey Line

The survey site chosen provided a range of soil gas concentrations from low levels of what are probably not geothermal gases (TH-1 and TH-3) at the "cold" west-SW end (downhole temperature approx. 30°C) to high concentrations of geothermal gases (TH-9, TH-10, and TH-11) at the "hot" east-NE end of the line (downhole temperature approx. 98°C). In between these extremes the downhole temperature rises gradually, except for a 75 degree spike at TH-6 and then a final rise to boiling at TH-9. This same pattern was also observed in the ground temperature study conducted at the same site in 1989-1991 (M. Mongillo, pers. communications, 1992).

Between the hot and cold ends of the survey line, gas levels do not reflect the gradual temperature rise or the temperature spike at TH-6. Instead the levels remain relatively constant with the exception of a small bump at TH-3. This behaviour can be related to the mechanisms for heat discharge through soils in thermal ground. According to Allis (1979), conductive heat flow becomes dominant below 60°C and convective heat flow above 80°C with a transition zone between 60° and 80". The patch of hot ground covered by the east-SE end of the soil gas line (TH-9, -10, and -11) represents convective heat flow resulting from a high steam and gas flux through highly permeable soil. Holes TH-1 to TH-8 are in ground dominated by conductive heat transfer between adjacent soil particles and the steam and gas flux from the underlying, shallow aquifer has become negligible. Soil gases in this area would be controlled by surface and near surface conditions and are probably a mixture of atmospheric and biogenic gases with the former being dominant. Any geothermal component would only be present at very low levels. The graphs for CO₂ and He in Figure 3 support this conclusion. Mass number 44, which represents CO₂, just about disappears in this region so the most abundant mass number 28, which can be the CO₂ ion fragment CO⁺ or N₂, must therefore be N₂. Helium, which is often used as a soil gas tracer for geothermal systems (Hinkle, 1991) remains at a nearly flat level in this conductive heat region, showing an increasing concentration only in the hot spot area. There is no clear cut transitional zone on this survey line, although TH-12 may be located in such a zone. More holes with a closer spacing than 10 metres might reveal a transitional zone.

The presence of COS and benzene are hard to explain from a geothermal context, but were included here to illustrate the

wide range of gas concentrations as well as gas species that the mass spectrometer can detect. The most abundant gas detected in the samples, CO₂, was four orders of magnitude (10,000 times!) more abundant than these two gases. We could also have included other gases at similar levels, such as CS, and SO, as there were mass peaks corresponding to their mass numbers on spectra from some of the sites. There is some precedence for including COS and CS, as these gases were the basis of a soil gas survey in the Roosevelt Hot Springs area of Utah, USA, conducted by Hinkle and Harms (1978). Although the benzene graph shows a relatively large peak in the hot ground area, it may not be related to gas migrating from the depths as much as some remnant from one of the more usual occupants of the sample site paddock that is slowly cooking away.

6. CONCLUSIONS

This investigation has shown that the portable quadrupole mass spectrometer is a suitable instrument for field use in soil gas surveys and with care can be directly connected to a sample hole for "real-time" analysis. Used in this was its main advantage is better management of the survey; it lets you see where you've been and where you are going. It also proved to be not as fragile an instrument as might have been expected and stood up well to the rigors of field work.

As would be expected, carrying-out the field work resulted in a number of ideas for improvements to the equipment. One draw back with the mass analyser system is the need for a vehicle to transport it to the survey site and to move it along the survey line, restricting surveys to vehicle accessible sites. If the mass spectrometer, power supply and batteries were available in smaller and lighter versions, back-packing the equipment to less accessible sites might be possible. With the present system, between 10 and 15 holes could be drilled and sampled in one day. The most time consuming tasks were hand-drilling the hole and waiting for thermometer probe to equilibrate with the downhole soil temperature. A small petrol driven auger (no bigger than a small chain saw) would speed up the drilling. Overcoming the temperature probe lag time might be more difficult. On a subsequent survey, we had four temperature probes and tried to keep 3 drilled-holes ahead of the working hole so temperature probes could be equilibrating in these holes. Equilibration could also be speeded-up if the probe were sheathed with a thinner and better heat conducting material than the fibre glass cladding used in this study.

The analysis in "real-time" capability of this sample probe-mass spectrometer system suggested that this would be a good system to use in a search for buried faults in geothermal areas, especially when there were no surface indications of the faulting. The resulting plots of soil gas levels along a survey transect perpendicular to the suspected fault line might look similar to the graphs in Figure 3, although the "fault gas" spikes would not be expected to be of as great a magnitude as levels reached over the hot ground. As the Rotorua Geothermal Field has a number of

suspected buried fault systems and funds were available for some additional soil gas work, a search for Rotorua faults has begun and the results will be reported at a later date.

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