GASSYS: A unique in-situ and passive gas sampling system from unsaturated soil and from groundwater

K. U. Weyer
WDA Consultants Inc., Calgary ,Alberta, Canada

M. Hamann
Chair of Applied Geology, University of Erlangen-Nuremberg, Germany

H. Kaiser
KaiserGEOconsult, Erlangen, Germany

Abstract

Sampling of soil air is applied by the oil industry in exploration and contamination studies. Techniques used range from active collection, where soil gas is gathered by pumping from a borehole, to passive collection over the course of 10 days or more on buried reactive carbon or similar materials as they are exposed to soil air.

Each of those sampling methods has its disadvantages. Active sampling draws soil gas from a large undefined space near the sampling interval. This results in preference to gas flow in higher permeable systems. Hence the results do not reflect the true and undisturbed gas content at the sampling interval. Passive sampling methods usually collect gases by adsorption onto solid material. Analyses using such sampling methods are limited to determining relative gas concentrations as no direct gas sample is taken.

The newly designed passive gas sampling system GASSYS overcomes the aforementioned disadvantages. It takes quantitative and reproducible gas samples from the unsaturated soil. Since the tube of the sampling chamber is permeable to gas but not to water, it also is capable of drawing gas samples from groundwater. Up to four sealed sampling intervals can be installed within an EVA-tube at depths to 30m and more.

In case histories gases from volatile and less volatile hydrocarbons were collected in the EVA-tubes for approximately 20 years without apparent loss of functionality.

Paper presented at the International Oil and Gas Conference, Zadar, Croatia, October 2-5, 2001

Introduction

Sampling of soil air is applied by the oil industry in exploration and contamination studies. So far applied techniques range from active collection where, from an active soil gas stream, samples are gathered by pumping and trapping soil gas in a collection chamber, as f.e. Tedlar bags or others, to passive collection on buried reactive carbon or other adsorbing materials when exposed to soil air over the course of usually 10 days or more.

Active vs. passive soil gas sampling

All current sampling methods have their disadvantages. Active sampling by pumping soil air into plastic bags or glass containers draws soil gas from a large undefined space near the sampling interval. This method results in sampling preference to gas flow in higher permeable systems. The application of a partial vacuum changes the soil gas content as volatile components with high partial pressure will, in response to the partial vacuum, transfer more material into gaseous phase than was gaseous before the application of the vacuum. Thus the results of active sampling do not necessarily reflect the true and undisturbed gas content at the sampling interval. Boreholes are usually sealed at the surface before soil air sampling commences.

A second method of active sampling by pushing a syringe into the bottom soil of short boreholes (Neumayr method, Germany) only records the contents in unsaturated soil, usually close to the surface. With this method boreholes are usually not sealed at the surface, possibly leading to contamination by surface air.

Thirdly, the installation of Dräger tubes in push-down drill rods reaches greater depth but is limited to pumping air from unsaturated soil as well (Dräger, 1994, p.47-50). Further complications are introduced by the consecutive use of several tubes each dedicated for a limited number of the components of the soil gas. Most tubes have limited concentration ranges and some allow only qualitative indication of contaminants.

Passive sampling methods usually collect gases by adsorption. Analyses using such sampling methods determine relative gas concentrations as no direct gas sample is taken. Presently they cannot be directly related to the actual concentration of contaminants in the soil air. In many cases this may not be important for the practical conclusion that the soil air is contaminated by a specific contaminant. Klein and Blumhofer, 1996, compared an active collection method (Neumayr method) with the passive methods used by Gore and by TerraGaz. They came to the conclusion that the results of all three field tests were the same in their tendency to indicate a relative degree of contamination. For the conditions of the sampling site Lichtenau, all three methods were thus principally suited to indicate the occurrence of contamination.

The investigation at this site bore another result. Surprisingly, the passive methods were able to detect BTEX at 9 sampling sites each (albeit not the same once) while the active Neumayr method detected BTEX only at one of the 15 sampling sites.

It appears that all methods listed above have limitations. The active Neymayr-method allows one-time sampling only at the bottom of an open borehole, the active Dräger method requires multiple sampling at a single sampling interval, the passive methods of Gore and TerraGaz allow only one time integrated sampling at a relatively shallow predetermined depth (50 cm to a maximum of 300 cm depth). All four methods are not well-suited for long term sampling under controlled conditions as they require new hole installations for each sampling event.

GASSYS

Many of the above shortcomings are eliminated by the new passive gas sampling system GASSYS.developed by KaiserGEOconsult GmbH, Erlangen, Germany, (Kaiser and Schillinger 1999). It can sample repeatedly and over many years from exactly the same position and under exactly the same sampling conditions within saturated and unsaturated soil, and it can determine the actual gas concentration per volume of soil gas. Sampling intervals can be installed at depths of 30m and greater. This method opens the door to controllable gas sampling conditions in the subsurface and the monitoring of gas components of chemical and biochemical processes in groundwater and soil air as they occur during natural attenuation, for example.

Fig. 1 Membrane tube used in GASSYS [modified after Kaiser and Schillinger, 1999, Fig. 1]

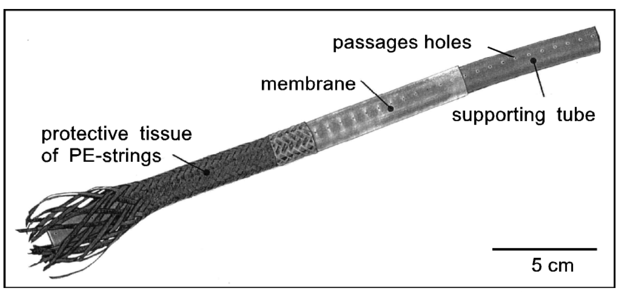
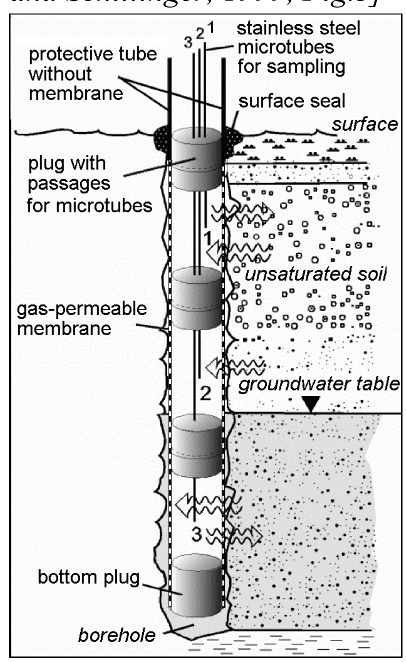


Fig. 2 Field installation of GASSYS with three sampling chambers [modified after Kaiser and Schillinger, 1999, Fig.3]



GASSYS collects, by diffusion through a permeable EVA (ethylene-vinyl-acetate) membrane quantitative gas samples from unsaturated soil into a tube (see Fig. 1 and 2). Since the membrane is permeable to gas but not to water, it also collects qualitative gas samples from groundwater.

During passage of gas through the membrane some gas particles are incorporated into the membrane until it is saturated with respect to gases passing through. The speed of diffusion processes depends on concentration gradients and thereby also on the availability of gas molecules at the outer wall of the membrane. We suspect that therein lies one of the reasons why we were thus far unable to draw gas samples quantitatively from groundwater. Due to diffusion the concentration drops in the part of the groundwater close to the GASSYS collection chamber. If the groundwater flows slowly the delivery of absorbed gas to the membrane is limited whereby not enough gas would be locally available to create a proper equilibrium with the contaminant concentration in the groundwater undisturbed by loss to diffusion. The matter is under further investigation.

The installed membrane tube stays in the ground and, in case histories for leak detection, has proven to function for more than 20 years for the collection of volatile and less volatile hydrocarbon gases. Within each tube up to four sealed sampling intervals can be installed at different depth (see Fig. 2). The diffusion collects gas samples from the space immediately surrounding the collection chamber. During sampling gas collected in the chamber is transferred from each segment by means of fine stainless steel tubes and calibrated syringes into a headspace vial. These vials are subjected to laboratory analyses.

The characteristics of the diffusion process are determined by the laws of Dalton, 1805; Henry,1802: Fick, 1855; and Raoult,1887, and the composition of absorbed gases, solutes, and solvents present at the outside of the collection chamber. The interrelationship of the various processes acting in the subsurface is subject to ongoing field and laboratory investigations.

Functionality tests of the GASSYS gas collection system

So far GASSYS has been tested for its functionality with respect to

- the kind of gases passing through the membrane,
- the diffusion times of soil gas and gas in groundwater into the sampling chamber,
- the adsorption of gas molecules onto the walls of a polyethylene and a steel tubing transferring the collected gas into an evacuation syringe,
- the reproducibility of the sampling procedure and the gas chromatographic analysis of gases collected,
- release of C1 to C4 hydrocarbons from manufactured EVA material, and
- removal of hydrocarbons from the matrix of the EVA tubing upon removal of outer diffusion source.

Gases passing through the membrane

RWTÜV and TÜV-Bayern, 1989, have provided a list of gases which were sampled for using the EVA tube subsequently used for GASSYS (compare Table 1).

Table 1: Gases sampled within EVA collection tubes (after RWTÜV and TÜV-Bayern, 1989)

acetone	chloropicrin	ethanol	heating oil	propane
acrylonitrile	crude Oil	ethyl acetate	n-hexane	iso-propanol
ammonia	cyclohexane	ethene	hydrogen	phenyl methanol
benzene	cyclohexanone	ethylene oxide	hydrogen sulfide	styrene
n-butane	dibutyl ether	formaldehyde	methane	tetrachloroethene
iso-butane	dichloroethane	freon-11	methanol	tetrahydrofuran
butanol	dichloroethene	freon-12	methyl acetate	toluene
butanone	dichloromethane	freon-21	methyl ethyl ketone	trichloroethane
butyl acetate	diesel fuel	Freon-113	methyl mercaptan	trichloroethene
carbon Dioxide	diethyl ether	freon-502	nitrogen dioxide	trichloromethane
carbon Monoxide	dimethylamine	gasoline	n-pentane	vinyl chloride
chlorine	dioxane	halon-1211	pentanol	xylene
chloromethane	ethane	halon-1301	pentyl acetate	

Diffusion times for hydrocarbons

<u>GASSYS in unsaturated soil</u>

Laboratory test data for gas from unsaturated soil established the diffusion/time characteristics for a gas mixture of methane, ethane and propane with complete equilibrium times between approximately 6.5

Figure 3: Diffusion of methane, ethane and propane from a bottle into an inserted EVA tube. During the diffusion test the concentration in the bottle changed in response to losses of material to the collection chamber of the EVA tube (after Faber et al., 1998, Fig. 6).

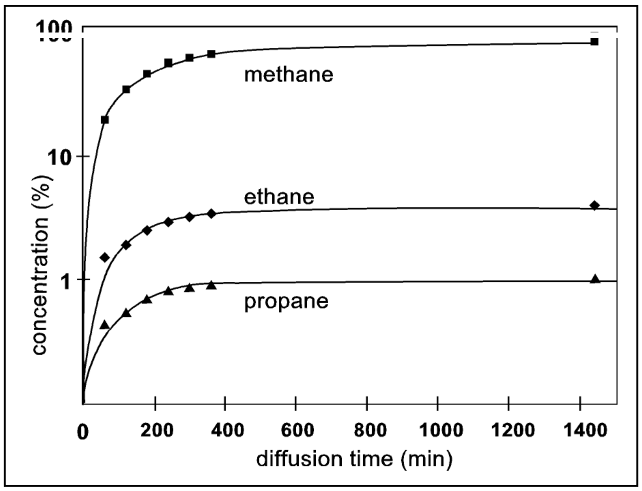


Table 2: Gases of chloronated hydrocarbons and BTEX sampled from water during static laboratory tests. [Data from M. Hamann, University of Erlangen-Nuremberg]

substances disolved in water -solubility increased by adding methanol; DIN 38407-F9 /F5 - **(µg / l)**		**gas sampled in chamber (µg / l)**
1,1-dichloroethene	132.99	2.26
trichloromethane	171.55	0.15
tetrachloromethane	116.28	0.11
1,1,1-Trichloroethan	91.76	0.22
trichloroethene	193.15	0.13
1,2-dichloroethane	166.58	0.09
benzene	9.47	1.26
toluene	7.74	0.64
ethyl benzene	6.91	0.34
p-xylene	7.00	0.27
m-xylene	6.74	0.27
o-xylene	7.03	0.22

and 10 hours (see Fig. 3). The concentration of gases outside the EVA-membrane was comparatively low and was not kept constant. Hence the diffusion process slowed down when the concentration of gases outside of the sampling tube was lowered due to the ongoing diffusion process. Gases moving into the EVA-tube were detected within 0.5 hours of installation.

In general the time to reach equilibrium of the gas concentration in the sampling chamber with the gas concentration in the unsaturated soil is related to the size, shape, polarity and the Brownian Motion behaviour of the gas molecules and the degree of saturation of the penetrated EVA material with respect to the migrating gases.

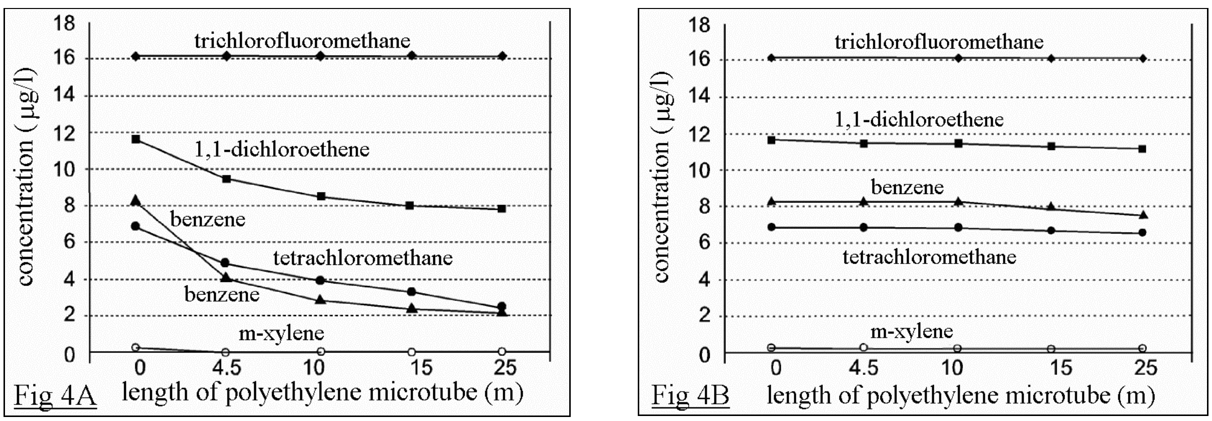
<u>GASSYS in water saturated environment</u>

Tests for diffusion of hydrocarbons from water saturated environments into the GASSYS gas collection chambers have been undertaken at the University of Erlangen-Nuremberg. They confirmed the seemingly erratic diffusion rates of contaminants from a water saturated environment into the collection chambers of GASSYS (see Table 2 and section "GASSYS" above for discussion of possible causes). Similar behaviour had previously been found in field tests at Lake Hallstatt in Austria (see Table 4 below).

Loss of gas by adsorption onto walls of delivery tubes

Two types of tubes have been tested with respect to loss of gases by adsorption during transfer of gases from the collection tube to the evacuating syringe, namely polyethylene tubing and stainless steel tubing. Figure 4A documents the pronounced loss experienced within polyethylene tubing by adsorption of gas molecules on the wall and penetration of gas molecules into the material of the wall. The amount and speed of penetration depends on the volatility and polarity of the gases flowing through the polyethylene tube. Figure 4B shows the sampling through steel micro-tubes to be nearly free of losses due to adsorption. Unfortunately, at the time, testing had to be done through 2m pieces of steel tubing which were connected to achieve the tested length. The break in slope in the curves for 1,1-dichloroethene, benzene, and other species *not* shown here may indicate that some of the couplings may not have been perfectly sealed.

Figure 4: Measurement of adsorption losses in tubes of polyethylene [A] and stainless steel [B]. [Data from M. Hamann, University Erlangen-Nuremberg]



Reproducibility of the sampling procedure and the gas chromatographic analysis

The reliability and reproducibility of the evacuation of gas by syringes from the sampling chamber through the steel micro-tubes, the subsequent discharge of the gases into headspace vials, thence into the gas chromatograph and the final analyses were tested by repeating the procedure 10 times for the chlorinated hydrocarbons 1,1-dichloroethene, trichloromethane, trichloroethene, 1,2-dichloroethane, and tetrachloroethene. Table 3 lists the results of the analyses. For each species the results of the 10 analyses were narrowly grouped and, for the various species, showed standard deviations from 0.11 to 0.17 or 0.8 to 1.8 % of the average values only (see Table 3). Hence, the gas handling procedure from the GASSYS sampling chamber to and including the gas-chromatographic analysis is reliable and reproducible.

Table 3: Results of 10 consecutive sampling events and immediately following analyses procedures [Data in µg / l from M. Hamann, University Erlangen-Nuremberg]

Test	1,1-dichlororethylene	trichloromethane	trichloroethene	1,2-dichloroethane	tetrachloroethene
1	18.49	14.20	9.29	12.76	5.90
2	18.67	14.34	9.53	12.96	6.17
3	18.33	14.11	9.35	12.73	6.05
4	18.05	14.00	9.22	12.54	5.94
5	18.32	14.11	9.35	12.68	6.03
6	18.27	14.07	9.31	12.68	6.03
7	18.34	14.15	9.34	12.77	6.21
8	18.41	14.15	9.34	12.74	6.07
9	18.28	14.11	9.28	12.66	6.19
10	18.10	13.94	9.02	12.44	5.93
Average	18.33	14.12	9.30	12.70	6.05
Maximum	18.67	14.34	9.53	12.96	6.21
Minimum	18.05	13.94	9.02	12.44	5.90
standard deviation	0.177	0.107	0.126	0.140	0.112
% of average	1.0	0.8	1.4	1.1	1.8

***Release of C1 to C4 hydrocarbons from manufactured EVA material*.**

Chemterra International Inc., 2001, of Calgary ran a test series to determine the release of C1 to C4 hydrocarbons from new EVA-tubes used in GASSYS. They did not find any release of C1 to C4 hydrocarbons at all. These results indicate GASSYS to be suited principally for exploration studies of gases emanating from petroleum reservoirs to the surface.

Removal of hydrocarbons from the matrix of the EVA tubing upon removal of outer diffusion source

Upon removal of a source of gas for diffusion into EVA-tubes the concentration of the gas within the EVA-tubing is reduced by diffusion of the gas from the EVA-tube towards the outside. The process

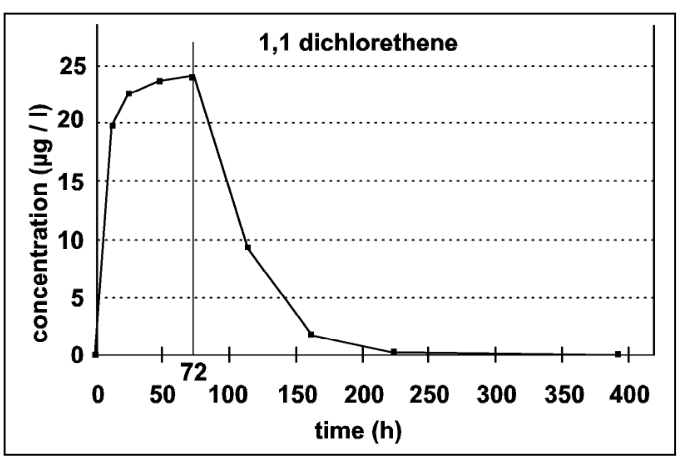


Figure 5: Diffusion of 1,1-dichloroethene into a GASSYS gas collection chamber with gas present at the outer wall of the membrane [hours 0 to 72] and lowering of 1,1-dichloromethane concentration in GASSYS collection chamber [hours 72 to 400] after the source of 1,1-dichloroethene has been removed from the outer wall of the membrane. [Data from M. Hamann, University Erlangen-Nuremberg]

is slowed down by the simultaneous removal of gas molecules from within the wall of the tubing. Figure 5 shows as an example the behaviour of 1,1-dichloroethene. From the start of the experiment until hour 72, the gas moves into the tube by diffusion. From hour 72 to hour 400, the gas moves out of the EVA-tube by diffusion after the gas has been removed from the outside of the tube. The delays in removal of gases from the EVA-tube need to be considered if tubes are to be reused in laboratory tests. These lag times are, however, not important for field measurements under their typically slowly changing environmental conditions.

Field tests of GASSYS

A number of field tests have been conducted in Europe by governmental agencies, Universities, and companies. The Bavarian Landesgewerbeanstalt (LGA) conducted tests for the Bavarian State Department for Landplanning and Environment at the waste disposal site Herzogenaurach, close to Nuremberg (Bavaria, Germany). The Craoatian oil company Industrija Nafte d.d. (INA), Zagreb, has been conducting tests with crude oil, diesel, gasoline and other products at the Etan refinery in Ivanićgrad near Zagreb. The German Geological Survey (BGR) tested the membrane tube's ability to collect gas from water and from lake sediments in Lake Hallstatt in Austria. The Chair of Applied Geology of the University Erlangen-Nuremberg has been conducting tests at a former military airport in Germany. Presently the system has also been commercially installed at another military airport in Germany. The Wismut AG in Germany recently installed GASSYS at a mine dump.

Sanitary and industrial landfill Herzogenaurach

During 1998 and 1999 the Bavarian Ministry of Landplaning and Environment sponsored a practical research project dealing with the collection of volatile gases of haloginated hydrocarbons at the landfill site Herzogenaurach (IUA-LGA and KaiserGEOconsult, 1999). Three GASSYS air wells were installed under unsaturated conditions up to 14 m depth. Two additional GASSYS wells were installed under saturated conditions within boreholes to depths of 18 and 20 m. 49 samples were taken during three sampling events for the unsaturated soil air wells and during two sampling events for the gas wells with diffusion chambers in groundwater. The analyses covered the following haloginated hydrocarbons: [1] dichloromethane, [2] trichloromethane, [3] 1,1,1-trichloethane, [4] tetrachloromethane, [5] trichloroethene, [6] tetrachloroethene, [7] cis-1,2-dichloroethene, [8] 1,1,2-trichlorotrifluoroethane, [9] dichlorodifluoromethane, and [10] trichlorofluoromethane.

The results for the components [5], [6], [7], and [9] were used for comparing the results of the various soil air well types and collection procedures. The investigators concluded that measurements with GASSYS showed excellent correlation and were reproducible. They also concluded these measurements to be reliable.

Pilot project Refinery Etan

The Croatian oil company Industrija Nafte d.d. (INA), Zagreb, has been conducting a pilot project at the refinery site Etan in Ivanićgrad near Zagreb. Various hydrocarbons were injected including crude oil, diesel, gasoline, and others. Results indicated that, under the conditions of the pilot project, even small amounts of low volatile hydrocarbons were detected by GASSYS. Novačić et al., 2001, report details of the results elsewhere in this issue.

Lake Hallstatt

In the context of scientific investigations the German Federal Geologic Survey (BGR) tested methane sampling with the EVA-tube of GASSYS in water depth of up to 126 m at Lake Hallstatt in Austria. Table 4 lists the amounts of methane collected from water and sediments of Lake Hallstatt (Poggenburg, 2001). Again, there are, so far, no clear pattern obvious explaining the causes for the seemingly unpredictable relations between the concentrations in the Lake water and saturated sediments outside and the amount of gas collected by diffusion in the EVA-tubing. Nevertheless the occurrence of methane was indicated in all tests. At a depth of 126 m ambient pressure exceeded 12 bar without collapse of the tubing containing atmospheric pressure. Thus when assuming a density of approximately 2 g/cm^3 for soil, GASSYS could be installed within rock at depth exceeding 60 m without collapse of the membrane tubing system.

Table 4: Methane sampling in Lake Hallstatt, Austria (data from Poggenburg, 2001)

	position of sampling intervall	position of gas sampling chamber	water depth [m]	diffusion time [h]	methane in sampling-chamber [µg/l = mg/m^3]	methane in nearby water or sediment [µg/l]
1	deepest point of lake	within water	126.0	24	0.04	0.20
2	Gossau jetty	on bottom	0.2	27	0.02	2.93
3	Gossau jetty	in sediment	0.2	23	0.08	2.93
4	Gossau jetty	in sediment	8.2	23	5.73	---
5	Lunz, 20 m from jetty	in sediment	10.0	30	1.89	2.09

Ongoing investigations at military airports and at a mine dump site

GASSYS gas collection systems have been installed at two military airport sites in Germany. In an effort to determine O_2-concentrations in soil air Wismut AG in Germany recently installed GASSYS at mine dumps of broken rocks. All three investigations are ongoing and cannot yet be reported on in detail.

Case histories of EVA-membrane tube

Starting in 1978 the Erlangen Research Centre of Siemens AG developed the subsurface Leak Detection and Location System LEOS ® making use of EVA-tubes. The same tubes are now used for the gas sampling system GASSYS. Therefore any experience at installations of LEOS by the Power Generation Section of Siemens AG at sites of companies like BASF, BP, VEBA, Ruhr Oil, Höchst-Iberica, Infracor Degussa-Hüls, Ciba-Geigy, Du Pont, Transpetrol, BSL/Dow, Koncern Naftowy - Poland, the airports at Oslo, Geneva and Zurich demonstrate the successful use of this permeable membrane tube for more than 20 years without known failures. It has been installed at product lines, oil pipelines, municipal gas supply lines, at chemical-warehouses, industrial facilities and landfill sites. Hübner, 2001, has summarized details of experiences gained elsewhere in this issue.

References

Chemterra International Inc., 2001. Oral communication to K.U.Weyer.

Dalton, J, 1805. On the absorption of gases by water and other liquids. Memoirs of the Literacy and Philosophical Society of Manchester, Second Series, v.1, p. 271-287

Dräger, 1994. Dräger-Röhrchen Handbuch (Dräger tubes manual). 9th edition, 380 p.

Faber, E., A. Hollerbach, H. Kaiser, J. Poggenburg, M.Hübner, W. Stahl, and H.J. Tobschall, 1998. Permeable Membranen – Ein Werkzeug zur vereinfachten Probenahme von Kohlenwasserstoff-Gasen? (Permeable membranes – a tool for simplified sampling of hydrocarbon gases). DGMK – Deutsche Wissenchaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V. (German Scientific Society for Petroleum and Coal), Proceedings of Annual Spring Meeting, Celle (Germany), April 1998, Report 9801, 10 p. (in German)

Fick, A., 1855. Ann. Physik, v.170, pp.59, Leipzig.

Hübner, M., 2001. Leos Leak Detection and Location System. This issue.

Institut für Umweltgeologie und Altlasten der Landesgewerbeanstalt Bayern (IUA-LGA) und Kaisergeoconsult GmbH, 1999. Erprobung eines segmentierten Gassammelsystems für horizontbezogene Gasprobenahme in Wasser und Böden von bereits untersuchten Arealen (Testing of a segmented soil gas sampling system for unsaturated soil and groundwater in areas with known contamination). Final Report of a Research Project prepared for Bavarian Department for Land Planning and Environment, Munich, January 1999, 65 p.

Kaiser, H. und Schillinger, C., 1999. Passives Gassammelsystem für horizontbezogene Gasprobennahmen in Böden und Grundwasser (Passiv gas measurements in soil and groundwater). TerraTech v. 6, p.19-21.

Kern, F., und W. Blumhofer, W., 1996. Vergleichsmessungen mit aktiven und passiven Bodenluftuntersuchungsmethoden in Lichtenau (Comparative measurements of active and passive sampling methods and analyses of soil air in Lichtenau). Handbuch Altlasten und Grundwasserschadensfälle, Landesanst. für Umweltschutz Baden-Würtemberg, 72 p.

Novačić, M., D. Crnčević, and T. Juranić, 2001. Hydrocarbon leak detection and continuous monitoring – Pilot project at ethane plant, Ivanićgrad. This issue.

Poggenburg,J., 2001. Written communication to H.Kaiser. Bundesanstalt für Geowissenschaften und Rohstoffe (German Federal Geological Survey), May 16, 2001.

Raoult, Francois-Marie, 1887. Loi generale des tensions de vapeur des dissolvant. Comptes rendus des séances de l´académie des sciences, Paris, v. 104, p. 1430-1433. May 21, 1887.

RWTÜV and TÜV-Bayern, 1989. Gutachten zur Erteilung einer wasserrechtlichen Bauartzulassung für LEOS. (Consultants report for application of LEOS with respect to water rights. Prepared for Siemens AG, UB-KWU, UED 13, Erlangen, 150 p., May 31, 1989.

August 2001