

MOBILE ODOR TESTERS FOR SOILS OR GRANULAR MATERIALS

W. ANDLAUER, M. KOCHBECK, R. KÖRBER, J. GOSCHNICK
Forschungszentrum Karlsruhe, Institut für Instrumentelle Analytik
D-76021 Karlsruhe, Postfach 3640, Germany,
Phone: +49-7247-826078, Fax: +49-7247-824606,
E-mail: Wolfgang.Andlauer@ifia.fzk.de

1. Introduction

Localization and characterization of volatile organic pollutants in soils is the aim of a rapid on-site analysis. In order to evaluate the potential of an electronic nose for direct online detection of volatile soil pollutants. Model gas exposures and practical tests were performed using KAMINA, the Karlsruhe MicroNose with two different sampling assemblies in direct sniffing mode. Odor testing with an electronic nose is nothing else than gas analysis of usually complex gas ensembles in an integral manner. Contrary to the classical description of a gas mixture as a sum of components with individual concentrations the electronic nose detects the gas ensemble as an entity with an integral concentration. However, similar to human odor perception the integral can be quantitatively divided into components which themselves may be complex mixtures. Owing to the measuring principle all pollutants are detectable as long as their volatility makes them appear in the gas phase. Therefore the term 'odor' should be understood as a pollutant signature in the gas phase no matter whether the human nose can smell it or not.

The KAMINA is an electronic nose system originally developed for gas analytical applications in consumer products such as ventilation flap control in automobiles or automated cooking processes and private medical diagnostics. The concept and technical outfit of the KAMINA do not only take analytical demands into account but also aim at low costs, minimum spatial requirements, low power consumption, and low weight, which are all mandatory for the equipment of mass products. This also makes the KAMINA an attractive tool for on-site soil screening. One application of this kind could be the screening of soil for localizing soil patches contaminated with volatile organic pollutants. Screening can be carried out either above the soil surface or an in-depth analysis is possible. Even a depth profile analysis, presently under development, can be performed.

2. Measuring Principles And Technical Equipment

The sensory heart of the KAMINA is a gradient microarray of conductivity gas sensors [1] (see Fig. 1). Owing to the high sensitivity of the measuring principle nearly to all types of gases (except rare gases and nitrogen) metal oxide gas sensing is the most universal gas detection principle for volatile pollutants. It is based on a

monolithic metal oxide layer (SnO_2 or WO_3) divided into segments by a set of parallel electrode strips. The microarray consists of 38 individual sensor elements with different gas selectivity properties resulting from a special gradient technique. The operation temperature and the thickness of the gas permeable SiO_2 coating are varied across the sensor array to differentiate the sensor elements. Thereby a gradual variation of the sensing properties of the metal oxide segments is achieved, resulting in gas-characteristic conductivity patterns which allow gas recognition.

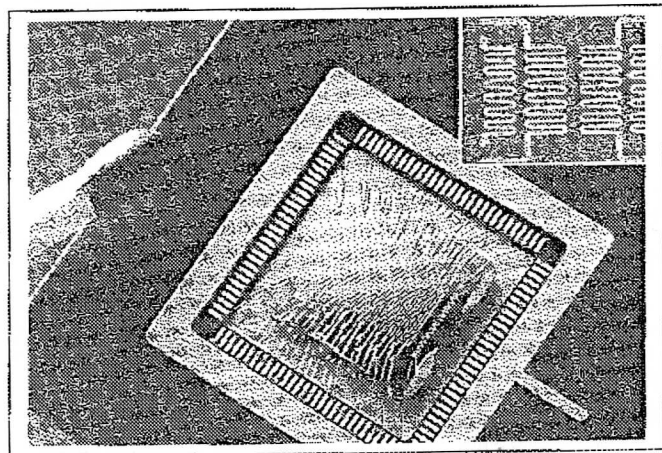


FIGURE 1. Gradient microarray chip mounted in its housing. The chip is based on a segmented metal oxide film of which the electrical conductivity is dependent on the ambient gas composition. A gas permeable SiO_2 layer deposited on top of the metal oxide with variable thickness across the array provides a different selectivity for each sensor segment. Two thermo-resistor strips beside the metal oxide film serve as temperature control. Electrical contacts are provided by thermosonic gold wire bonds. The rear side of the chip (upper right) carries 4 meander-shaped heating elements made of platinum to allow inhomogeneous heating of the chip.

First, the gas response of two microarray chips, one equipped with platinum doped SnO_2 (SP-type) and the other with WO_3 , was examined by exposing them to model pollutants under defined conditions. The results showed that for hydrocarbons and halocarbons the analytical performance of the SP-type of microarray chip was clearly the best, offering detection limits below 1 ppm, response times of a few seconds and an excellent discrimination by the conductivity patterns of the gradient microarray. A surface temperature gradient maintaining a difference of 250–300 °C across the array turned out to be the optimum operating condition.

The KAMINA is a complete electronic nose system the size of a beverage can comprising a special gas sensor microarray, a fan or a micropump for air sampling and all necessary electronics in one instrument. The gas sensing module is controlled via a standard serial interface by a standard PC operated under WINDOWS. The KAMINA managing software allows full control of the measurement of the gradient microarray, online visualization of all signals including data storage and online data processing. The latter consists of a variety of signal filter modules and a number of multivariate data evaluation tools to tailor an appropriate online evaluation of the nose data.

For surface restricted sniffing a mobile pumped extractor hood assembly was developed equipped with the KAMINA and a reference clean air source (see Fig. 2 a). The extractor hood has a quadratic opening (30x30 cm) which is placed on the ground surface to analyze the release of volatile soil components to detect surface contamination.

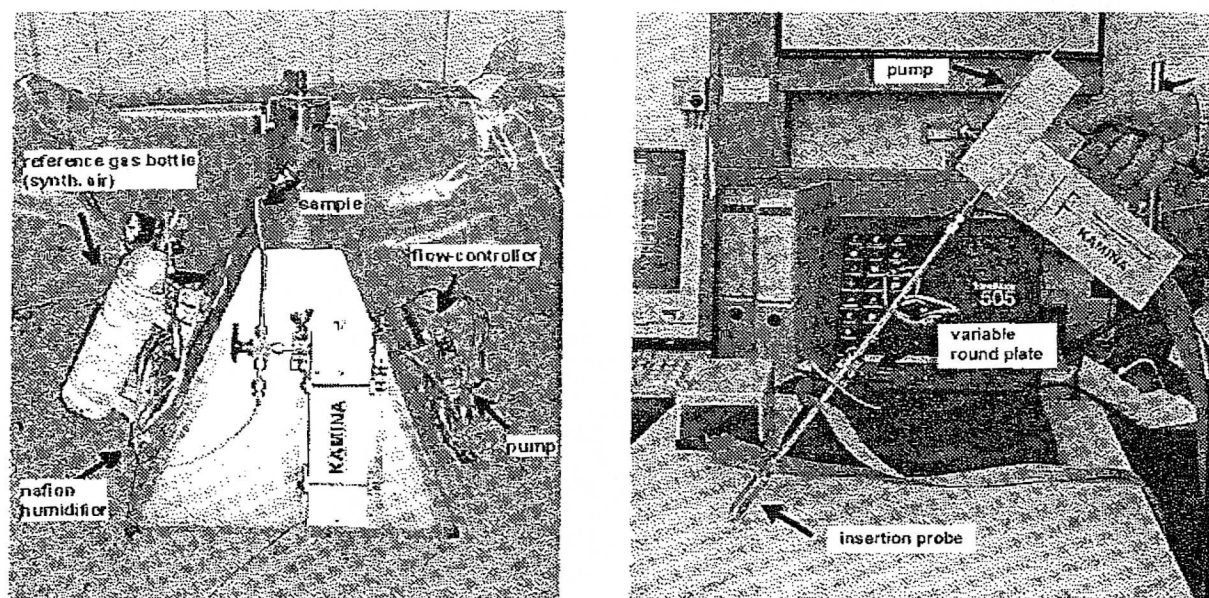


FIGURE 2. a) The left image shows the KAMINA equipped with the extractor hood for surface soil analysis. b) The right image shows the mobile handheld odor tester for in-depth analysis with an insertion probe.

For more local, and even in-depth, measurements of volatiles released from soft soils or piles of granular materials a portable KAMINA (see Fig. 2 b) was developed equipped with an insertion probe for sampling. The air inside the soil or granular beds is sampled with a stainless steel tube (ϕ ca. 15 mm) with side openings and a conical shaped end part to be inserted into the granular material. Through the side openings, shielded against dust particles by a fine metal gauze, the sampled air is brought to the microarray by an integrated micro-pump (max. 0.8 l/min gas flow rate) in the KAMINA head compartment. The air sampling flow can be adjusted by the software.

3. Results

The two types of soil sniffing devices have been investigated for their potential of direct pollutant detection with a number of model experiments conducted in containers filled with sandy soil at room temperature. The soil was artificially contaminated with toluene, methylene chloride and gasoline in different scenarios. The first study, which is reported on here, was restricted to single contamination (i.e., with one component only).

In order to examine the surface sniffing device with the extractor hood assembly, a $1 \times 1 \times 1 \text{ m}^3$ container was filled up to a height of 80 cm with soil. The soil surface was separated into 4 quadratic sections, 1 left uncontaminated, and 3 sections doped by deposition of the liquid model contaminants mentioned above (20 ml/0.25 qm). The hood, pumped with a flow of approx. 1.5 l/min, was sequentially placed upon the corresponding section to transfer the organic vapors with a carrier gas stream to the KAMINA for analysis. 2 min after the placing hood, the signals of the microarray had already become approximately stationary. In all three cases the electrical resistance of the 38 sensor segments dramatically decreased by about an order of a magnitude. The resistance decrease, typical of organic gases in metal oxide gas sensing [2], was of course slightly different at each sensor segment owing to the gradient principle of the microarray. The conductivity patterns obtained for each of the contaminated sections were evaluated with multivariate data analysis by Principal Component Analysis (PCA) to investigate the differences.

The results of the PCA are depicted in the plot of Fig. 3. Each position in the plot represents a certain signal pattern of the microarray. Although there is some scatter, the data points of the clean soil and the three contaminated soil sections cluster clearly in well separated areas. Obviously there are characteristic differences in the signal patterns of the three contaminants toluene, methylene chloride, and gasoline, which allow a clear distinction between them.

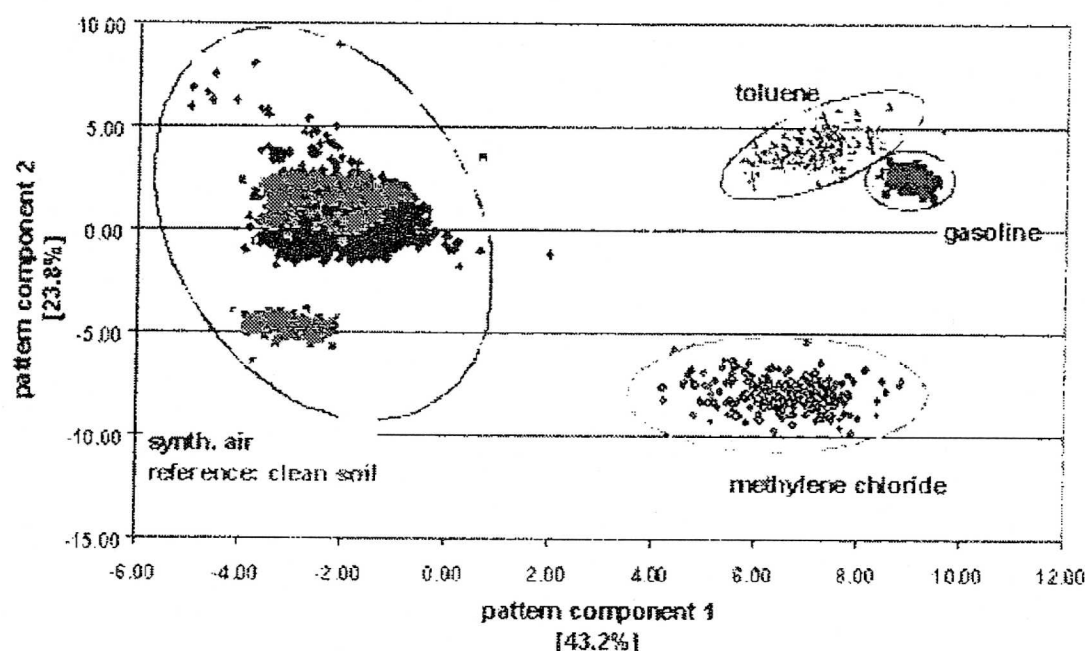


FIGURE 3. Principal Component Analysis (PCA) of conductivity pattern obtained by the gradient microarray shortly after placing the extractor hood on the soil (doped with the model pollutants toluene, methylene chloride, gasoline).

The handheld KAMINA equipped with an insertion probe is meant for the in-depth analysis of soils, although measurements in air (above the soil) are also possible. In order to examine the depth profiling ability a gasoline contaminated buried layer of sandy soil served as a model contamination structure. The latter was arranged by homogeneously spreading out a precontaminated soil of 0.5 ml/kg concentration with a thickness of 2 cm on top of clean soil. The contamination layer was buried by a further layer of clean soil with a thickness of 15 cm. After giving the model system 10 min for the gasoline contaminant to spread, the insertion probe KAMINA was applied to analyze the air at 4 depth positions. The first air analysis was performed directly above the surface, the others in depths of 5, 10 and 15 cm. The duration of the measurements was approx. 4–5 min before the probe was pushed to the next depth. Subsequent to the deepest measurement, the insertion probe was pulled out of the soil and the response to the air above the soil was again recorded. The results are shown in Fig. 4 depicting the 38 gas sensor resistances versus time during the test procedure. The typical response of metal oxide gas sensors to oxidizable vapors can be clearly seen. The resistances drop the more the higher the concentration is. Similar to the extractor hood KAMINA, it takes only 1–2 min of measuring time after positioning the probe in the soil to get constant signals. Obviously, it is no problem to detect concentrations far below the initial 0.5 ml/kg because a resistance change of nearly a magnitude is detected within the contamination layer although the settling after preparation has led to some spreading of gasoline, reducing the initial concentration of the precontaminated soil. Therefore, it can safely be estimated that the detection limit for gasoline in the sandy soil used is lower than 0.05 ml/kg.

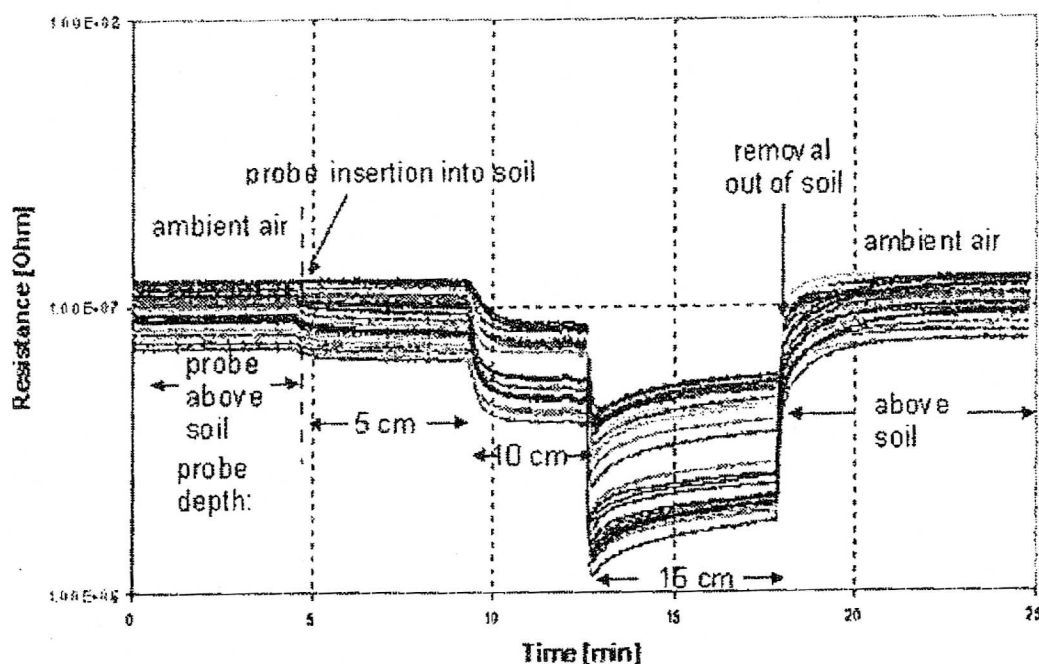


FIGURE 4. Depth-resolved investigation of a gasoline contaminated buried layer with the handheld KAMINA.

In a second test of the mobile odor tester a contamination patch was modelled. In this case toluene was mixed with sandy soil at a concentration of 0.5 ml/kg. This soil was brought into a hollow of clean soil situated in a container of 45x55 cm² and a depth of 15 cm. The hollow filled with the contaminated soil had a cylindrical shape and was 15 cm in depth and 7 cm in diameter. As can be seen from the schematic presentation of the analyzed area in Fig. 5b, the pollution center was asymmetrically surrounded by a thin polyethylene (PE) foil of low permeability for the toluene. The foil was placed vertically in the soil to impede pollution spreading in certain directions, enabling an unsymmetrical distribution of the toluene. After placement of the toluene polluted soil, 1 h was waited for prior to the start of the measurements with the insertion probe. With the pollution in its center, an area of 40x40 cm² was examined by 41 separate measurements at a depth of 10 cm each, taking only about 1 min. Thus, the whole investigation took no more than about 2/3 h.

The results are shown in Fig. 5a. The decrease in the median resistance, representing the response of all sensor segments, is depicted over the measuring locations. The three-dimensional plot clearly shows the decline in toluene concentration the further away from the pollution center the soil was probed. Obviously the waiting time resulted in some dissemination of the model pollutant. Moreover, the less steep decrease of the toluene concentration shows the expected effect that the toluene finds its way more rapidly through the area where spreading is not hampered by the PE foil. Hence the pollutant distribution can be easily determined by the insertion probe KAMINA. Moreover, similar to the first investigation of the mobile electronic nose the detection limit for toluene seem to be again better than 0.05 ml/kg or < 50 mppm. This is because the maximum concentration in the pollution center at the measuring time is definitely lower than the initial concentration there. On the other hand the measured median decrement of the resistances of the microarray elements is more than a magnitude above the noise level of approx. 0.3 MOhm (i.e., 3% of the clean air value of 10 MOhm).

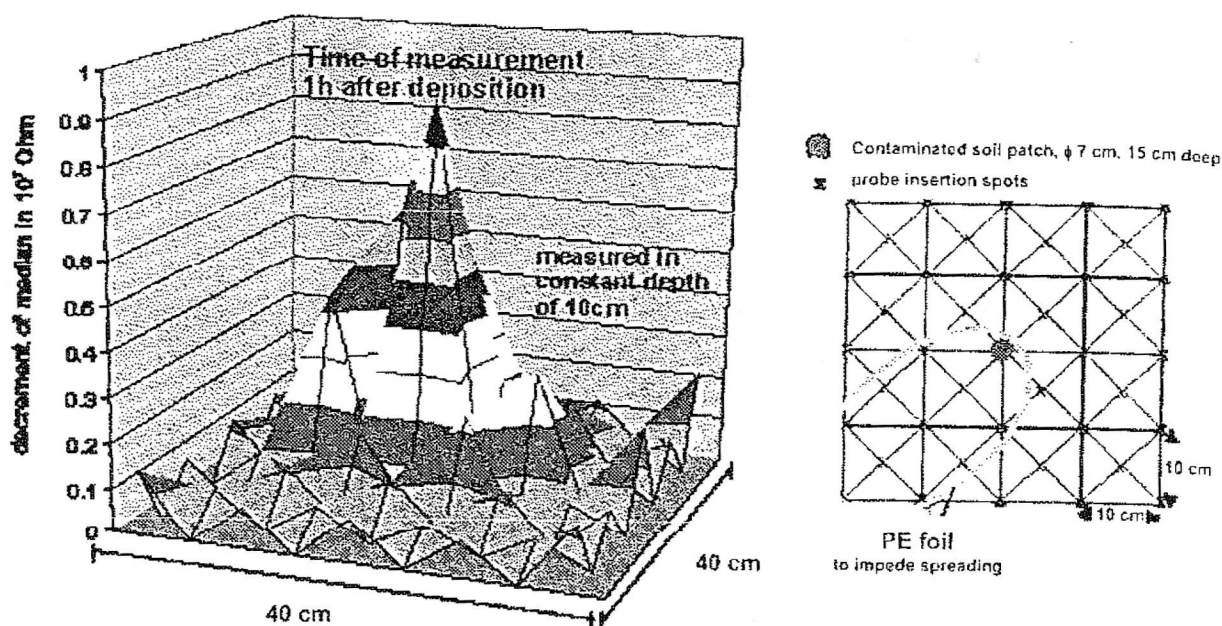


FIGURE 5. a) The left diagram shows the lateral localization of a toluene contaminated patch surrounded by clean soil. b) The right image shows the schema of the 41 measurements.

4. Conclusions

The electronic nose KAMINA equipped with a SnO_2 based microarray chip and appropriate sampling techniques has been successfully tested for direct soil screening. The mobile electronic nose device can easily be handled with its size of a beverage can. The special gradient microarray permits detection limits better than a few vppm and a response time of a few seconds for organic gases. For volatile organic pollutants being disseminated in sandy soil, the discrimination power was found to be appropriate to distinguish toluene, gasoline and methylene chloride. According to the experience obtained in fundamental investigations as well as in other application areas [1] this result can be generalized to be valid for most gases. The detection limit for direct on-site screening of gasoline and toluene in sandy soil was estimated to be better than 0.05 ml/kg or 50 mppm. Contrary to the gas detection limits the mass related detection limits depend on the type of soil, its morphological consisting and its temperature. A spatial resolution with the present insertion probe of < 5 cm could be achieved. The necessary time for testing one soil spot lies within the range of 1 min. Hence, according to this first results on soil applications, the electronic nose KAMINA has the potential for a powerful on-site soil screening device for rapid and effortless detection of volatile organic pollutants.

5. References

- [1] GOSCHNICK, J.: "An Electronic Nose for Intelligent Consumer Products Based on Gas Analytical Gradient Microarray "; to be published in *Microelectronic Engineering, Proceedings of the Micro- and Nano-Engineering Conference, Jena, 2000*
- [2] W. GÖPEL, K.-D. SCHIERBAUM: „Electronic Conductance and Capacitance Sensors“; in *Sensors, Vol.2 „Chemical and Biochemical Sensors“*; eds. W. GÖPEL, T. A. JONES, M. KLEITZ, J. LUNDSTRÖM & T. SEIYAMA; Verlag VCH, Weinheim, New York 1991, p. 429