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Diesel detection in surface water in the low ppb range

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Abstract

A method for diesel detection in surface water in the low ppb range is presented. Even though standard commercial metal oxide gas sensors with detection limits in the ppm range are used, extraction of volatile compounds from the water enables a detection limit of about 2 ppb diesel in the water. The technique can be used for surface water monitoring. The standard technique of ultraviolet fluorescence detection has an interference problem with humic substances. This is not a problem with the suggested technique. Results from lab measurements as well as field tests at a water utility in the Stockholm region in Sweden are presented.

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Keywords: Gas sensor; water monitoring; diesel detection; ppb range

1. Introduction

One of the concerns for waterworks is contaminations in the water supply. Waterworks using surface water are susceptible both to chemical and microbial contaminations. For example 5 ppb diesel in the surface water is enough to cause consumer concerns and costly measures have to been taken to remove the diesel contamination. The standard technique for petroleum detection in water is ultraviolet fluorescence (UVF). The technique suffers, however, from interference problems due to humic substances which impairs the detection limit.

We have previously presented a method for monitoring drinking water in distribution networks with a so called electronic tongue [1]. Here we present a new method for detection of volatile compounds in surface waters based on standard, commercial metal oxide gas sensors capable of ppb level diesel detection in water in field measurements.

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2. Experimental details

Fig. 1 shows a schematic illustration of the measurement setup. A valve can switch between a sample and a reference. The liquid is brought to a gas/liquid separation unit where the volatile compounds are extracted from the water and swept away to a gas sensor array by an air flow and the waste water is removed. The data of the gas sensor array is then evaluated with multivariate data analysis. We have been able to reach almost 100 % conversion of diesel compounds from the liquid to the gas phase and thereby reaching a detection limit of 2 ppb diesel in the water sample.

Measurements were performed both in the laboratory, with water samples from two different lakes, and at a drinking water production plant. The Görveln water utility outside Stockholm, Sweden, uses water from a nearby lake, Mälaren, that contains moderate to high levels of humic substances. These substances do not interfere with the diesel analyses, but may cause deposits and clogging of valves, tubes and the separator unit. Thus, a precaution step was taken in the field measurements by flushing washing liquid through the system for two minutes every six hours. The solution consisted of drinking water containing 50 g/l of machine washing-up liquid.

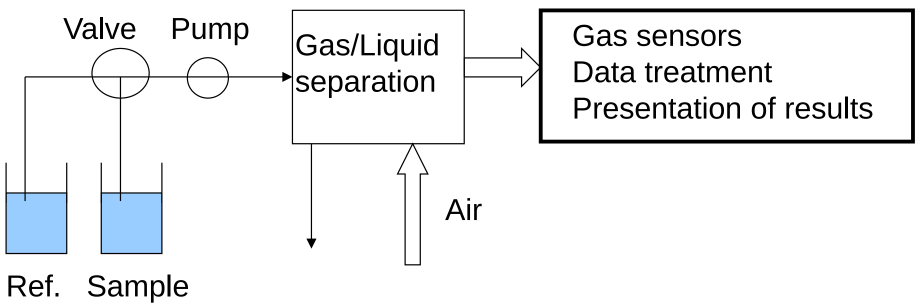

Fig. 1. A schematic illustration of the measurement setup.

3. Results and discussion

In Fig. 2 data from lab measurements of water samples from lake Vättern, Sweden, are presented in the form of a PCA plot of the data from the gas sensor array. Additions of ethanol and diesel at different concentrations result in clear separations of the data and in one diesel direction and one ethanol direction in the diagram. In the concentration range studied here the response roughly increases linearly with concentration.

Separate measurements have resulted in a detection limit of about 2 ppb diesel. This is below the target concentration of 5 ppb set by representatives of the water utility.

The PCA plot also shows the results of measurements of a sample from the harbor of the city of Motala at lake Vättern. The PCA puts these data along the diesel direction of the diagram. The data indicates that the water from Motala harbor is contaminated with about 60-70 ppb diesel.

In addition, similar measurements were performed with water from a second lake, Salstern, with much higher levels of humic substances. No indications of interference problems due to the different humic contents were observed.

The laboratory results motivated the construction of a more robust system intended for field measurements at a drinking water production plant. Such a prototype instrument for continuous monitoring of the intake water at the Görveln waterworks at lake Mälaren, Sweden, was built and installed.

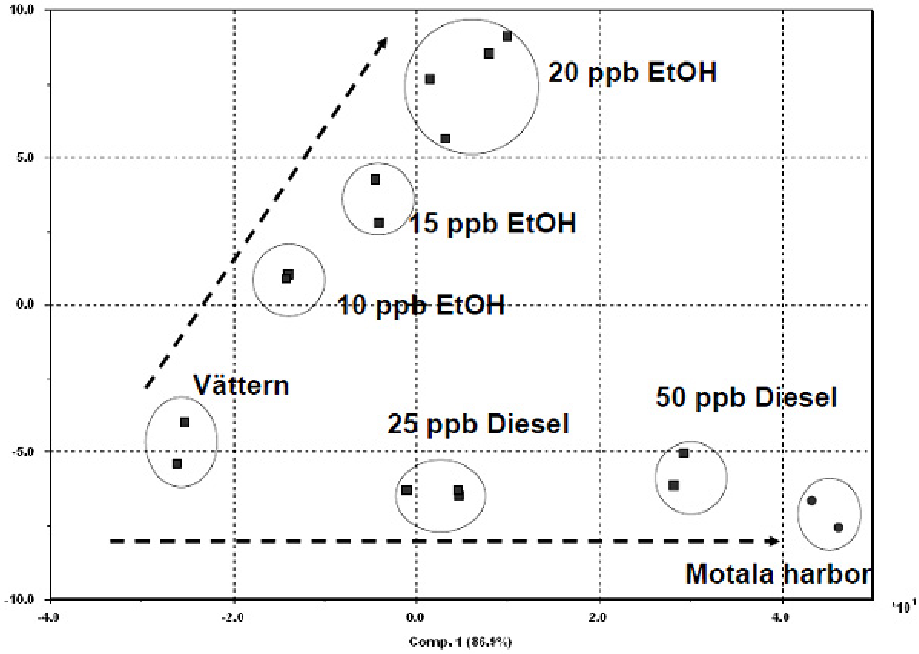

Fig. 2. PCA plot from lab measurements of water from the lake Vättern, Sweden, with different concentrations of diesel or ethanol (EtOH) added to the water. Also a sample of water from the harbor of the town Motala at the lake is included.

The instrument proved to be robust enough for long-term, continuous field measurements while detecting low concentrations, down to a few ppb, diesel in the raw water. Fig. 3 shows results from these measurements.

Fig. 3a shows raw data for the three sensors during normal measurement conditions. Every six hours a cleaning step is run, inducing a negative spike in the sensor data. The sampling time is 10 minutes and the cleaning step takes 2 minutes, so each cleaning step influences one data point.

Fig. 3b shows the result of a simple prediction of the diesel concentration based on the three sensor responses in fig. 3a. The predicted value is close to 0 ppb, as expected, except at the cleaning steps. The spikes could of course be compensated for or filtered out, but we have chosen to keep them as an indication of these cleaning steps.

Fig. 3c shows the sensor responses during addition of first 20 ppb diesel and later on 10 ppb diesel. In addition to the response to these diesel additions, the spikes induced by the cleaning steps influence the sensor signals as described above.

Fig. 3d shows the diesel concentration predicted from the data of fig. 3c. The negative spikes are still artifacts due to the cleaning steps and a few positive spikes are due to disturbances and to the inability to turn on the diesel addition as a perfect step increase.

These results show that the instrument is capable of diesel detection in the low ppb range also at field conditions.

4. Conclusions

The results show that the measurement setup is capable of detecting diesel concentrations in the low ppb range, both at laboratory conditions and during field measurements. The field measurements lasted for several months and the instrument turned out to robust and delivered stable results. The laboratory tests showed that the instrument can distinguish between diesel and ethanol. In fact, with additional gas sensors the instrument is expected to detect and discriminate low concentrations also of many other volatile compounds.

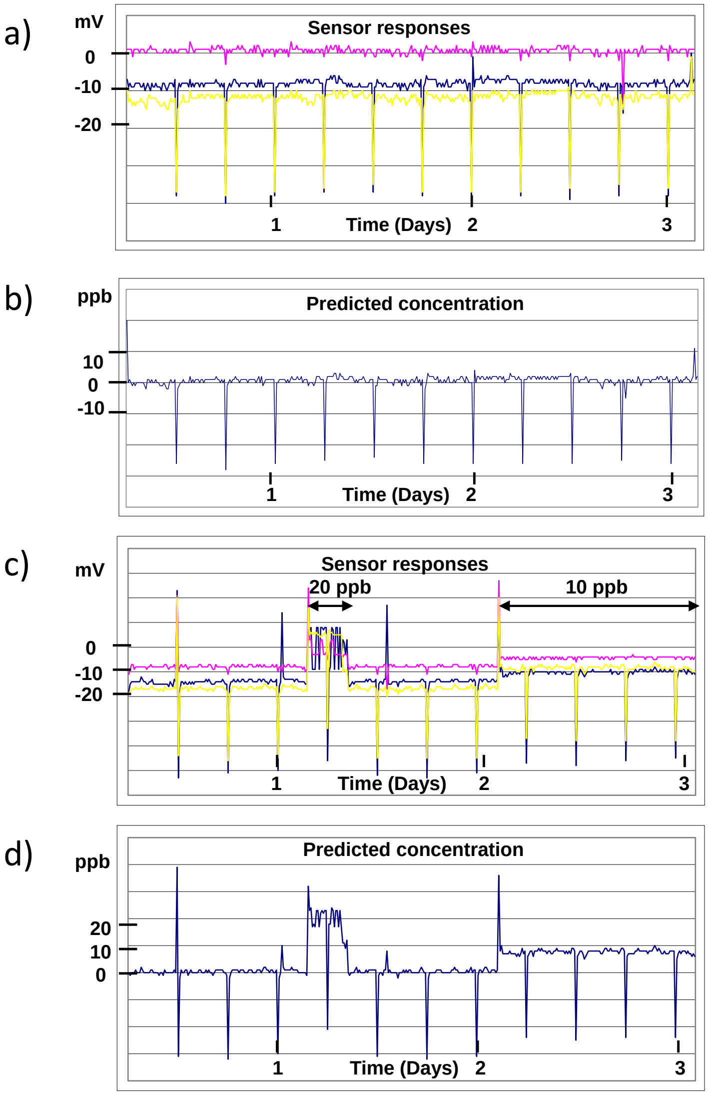

Fig. 3. Field measurements at the Görveln water works outside Stockholm, Sweden. a) Responses of the three gas sensors as a function of time. Every six hours a cleaning step is performed which induces a negative spike. b) Predicted diesel concentration from the sensor data in a). c) Sensor responses during addition of two different concentrations of diesel (10 and 20 ppb) as indicated by the arrows d) Predicted diesel concentration from the sensor data in c).

Acknowledgements

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