

## Final report VISTA 2014

### Project title

*Development of ultrasensitive methods for determination of nitramines in drinking water and soil for assessment of possible environmental impact of amine emissions from a CO<sub>2</sub> capture plant*

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Project number: 6160

### **1. ½ A4 page with a popular presentation of the project (to be written by the scholar)**

The aim of the project was to develop highly sensitive analytical methods for determination of selected nitramines in water and soil samples. Nitramines can be formed by atmospheric photo-oxidation of amines which can be emitted from CO<sub>2</sub> capture plants. Due to their possible carcinogenic/mutagenic effect it is important to have methods to monitor their possible presence in nature, *e.g.* lakes and soils. The proposed limit of nitramines in drinking water in Norway is in the ng/L range and to be able to measure such low concentrations, a highly sensitive detection method is needed. Most of the published methods in the literature today have a detection limit in the µg/L range for nitramines.

In this project methods for monitoring nitramines have been developed using a combination of liquid chromatography and mass spectrometry (LC-MS). Because of the expected low concentration of possible nitramines in the sample a pre-concentration step is necessary even using the most sensitive MS instrumentation. Solid phase extraction (SPE) was chosen for the pre-concentration as this method can be coupled on-line with LC-MS. Various SPE materials have been evaluated to pre-concentrate the polar nitramines from water, however our conclusion was that today there is no material available that can be used for co-extraction of both primary and secondary aliphatic nitramines. For primary nitramines, such as monoethanolamine, porous graphite carbon or anion exchange based material can be used, but with a prior desalting step depending on the sample volume applied. Secondary nitramines, *e.g.* dimethylnitramine, had a high adsorption on polystyrene-divinylbenzene based material. The pre-concentrated samples were analysed with reversed phase LC-QqQ-MS/MS. The detection limit of the nitramines in the LC-MS/MS method was 10-100 pg, which means that samples with concentrations of ng/L of nitramines need to be concentrated about 100x in the pre-concentration step. To improve the detection limit in the MS, different ion sources and additives in the mobile phase were evaluated. The conclusion was that for the instrument used, electrospray ionization was a better alternative compared to atmospheric chemical ionization, with negative and positive electrospray ionization for the primary and secondary nitramines, respectively. Regarding the mobile phase, better detection was achieved using methanol as the organic modifier compared to acetonitrile, and for pH

control acetic acid was better than formic acid, and only low concentration of acid should be used.

**2. Have there been any changes in the objective/goals during the project period? Did you achieve what was promised in the project description? (to be written by the scholar)**

There have not been any changes with the objective/goals, but we didn't manage to achieve and test everything stated in the project description.

The major deviation from the targets stated in the work schedule is that work with molecular imprinted polymers and the development of methods for soil samples were never initiated. The reason for this is that the time to evaluate support material and to develop separation and detection methods took longer time than estimated, partly due to the lack of appropriate LC-MS instrumentation in the beginning of the project.

**3. Publications (scholar)**

Lindahl, S., Brecke Gundersen, C. and Lundanes, E. *A review of available analytical technologies for qualitative and quantitative determination of nitramines*, Environmental Science: Processes & Impacts, 2014, 16, 1825-1840

Brecke Gundersen, C., Andersen, T., Lindahl, S., Linke, D., and D. Vogt, R., *Bacterial response from exposure to selected aliphatic nitramines*, conference paper/abstract, International Conference on Greenhouse Gas Technologies (GHGT)-12, 5-9<sup>th</sup> of October 2014, Austin, Texas, USA

Lindahl, S., has participated at the 21. Norske Symposium i Kromatografi (Sandfjord, Norway), with an oral presentation entitled: Development of online SPE-LC-MS methods for determination of nitramines in environmental samples.

**4. Reflections on continuation of the project (to be written by the project director)**

As written by the scholar we did not achieve all goals written in the proposal for the reasons given. These small polar nitramines present in polar samples as water present a huge analytical challenge. Their response in MS is also inferior to many other compound types. In the project we have found suitable material for pre-concentration of secondary nitramines, while it is still a challenge to find a good material for pre-concentration of the primary nitramines which have a pKa of about 6, without a pretreatment involving desalting of the sample. These challenges are most for the small monomethylnitramine and monoethanolnitramine, and less for the larger more hydrophobic nitramines.

At present our LC-MS method, which utilizes a C18-PFP (150 x 1.0 mm, 3  $\mu$ m) column and an injection volume of 1  $\mu$ L, with a mobile phase consisting of 1-2 mM acetic acid+methanol (1+1, v+v), can detect the primary nitramines at 50-100 ng/mL, and the secondary nitramines at 10-100 ng/mL in one analysis.

Lower detection limits can be achieved by performing the pre-concentration as described by the scholar, however, in this case separate methods are needed for primary and secondary nitramines. It should be noted that there is still a challenge to perform the pre-concentration on-line with the LC-MS, which is to be preferred in a lab handling many samples. More work is also needed to adopt the method for determination of low concentration of the nitramines in aqueous extracts of soil samples. At present we are using the LC-MS method for studying the adsorption of nitramines in soil samples and measurement of possible nitramine degradation by microorganism in lake samples or by bacteria in toxicity studies, however restricted to the concentrations possible to monitor without pre-concentration.

Since there is still a gap in methodology required to achieve detection limits in the ng/L range, more resources are needed to reach the goal. Our group cannot continue the method development project with the personnel resources available at the moment. Development of sensitive and robust methods for monitoring of the small and polar nitramines in aqueous samples requires highly skilled analysts who can dedicate their time to the challenge.