



Development of a diffusive sampler for ozone

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Abstract

Lower tropospheric ozone is an increasing problem and as a powerful oxidising agent, it causes health effects on plants and humans, it irritates the nasal cavity, the throat and the respiratory system. These potential risks emphasise the need to measure ozone at low levels but few passive sampling methods for measuring ambient ozone have been described. The GMD diffusive sampler can be used to measure ozone when using filters impregnated with indigo carmine, provided that the method is developed. Our aim was therefore to develop a passive sampling method to measure low ozone levels indoors i.e. to find a filter, a solution and an analysis method that suit the needs for a GMD diffusive sampler.

In this paper our work towards this working GMD diffusive sampler is described and the results from our experiments summarised. The final results of our work led to many conclusions and the definitive ones turned out as follows; Whatman silica gel loaded filters is impregnated with a solution of indigo carmine, methanol, tetrabutylammonium bromide (TBA), water and dichloromethane. While impregnating we used a method that includes a microinjection pump to coat the filters and a writer to regulate the speed of the filter. Analysing samplers with these filters that were impregnated in this way, gave useful results when analysing the samplers with Near Infrared Spectroscopy.

Preface

This paper is an examination work on the Science profile at Luspengymnasiet. The work has been done at the Department of Chemistry, Environmental Chemistry, Umeå University and the Center for Musculoskeletal Research, National Institute for Working Life, Umeå. Associate professor Barbro Andersson was supervisor.

Development of a diffusive sampler for ozone

1. Introduction

Ozone is an oxidant gas produced in a natural way in the Earth's atmosphere [1]. The stratospheric ozone is essential for the screening of solar ultraviolet radiation and a big environmental problem is that the stratospheric ozone is demolished by depletion. Anthropogenically emitted substances are one reason why the natural levels of ozone are depleted.

Lower tropospheric ozone is a result of natural and anthropogenic emissions of volatile organic compounds (VOC), nitrogen oxides and sunlight [2]. The level of lower tropospheric ozone is increasing and ozone episodes appear more frequently and with higher peak levels than before. In Sweden the environmental goal for the long-term average of ozone during the season of vegetation (April- September 09.00-16.00) is $50 \mu\text{g}/\text{m}^3$. In the south of Sweden this limit is exceeded by 50-70%. Ozone is a powerful oxidising agent and causes health effects on plants and humans, it irritates the nasal cavity, the throat and the respiratory system. Ozone can cause acute health effects after short-term exposure at levels higher than $160 \mu\text{g}/\text{m}^3$.

The potential risks emphasise the need to measure ozone at low levels. Few passive sampling methods for measuring ambient ozone have been described. Grosjean and Hisham presented a method based on the reaction of ozone and indigocarmine, (fig. 1) [3]. Scheeren and Adema continued this work in 1996 [4]. They used a coated glass filter (Whatman GF-A). After sampling the filter was removed from the badge and extracted with distilled water in an ultrasonical bath. The solution was analysed spectrophotometrically at 610 nm. The ozone level is established by calculating the difference between the amount of indigo carmine on the exposed filter and the amount on an unexposed filter. An exposure time of one hour resulted in a detection limit of about $45 \mu\text{g}/\text{m}^3$. Drawbacks of this method are the low amount of indigo carmine on the filter, which implies that the sampler cannot be used at higher ozone levels since the indigo carmine will be consumed. In addition the sampler is sensitive to wind, in general an average of approximately $0,5 \text{ m/s}$ is necessary.

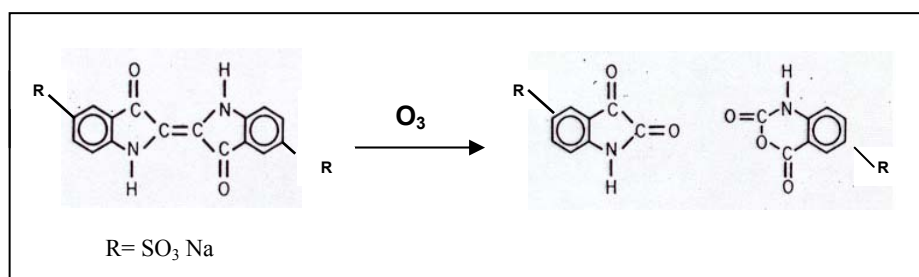


Figure 1: Reaction between indigo carmine and ozone.

There is a need for a passive diffusive sampler that can measure low ozone levels during a short time in indoor air. The sampler should be easy to prepare, handle and analyse. This paper describes a development towards this required sampler, based on the reaction above.

1.1 Diffusive sampling

1.1.1. Diffusive sampler

Diffusive sampling is a passive sampling method [5]. A passive sampling method implies that there is no need for a pump to suck air through the sampler, which makes the sampling much easier to accomplish.

1.1.2. Formula

The formula below is used to calculate the amount of the measured substance.

$$m = DctA/L$$

- m = The analysed amount (ng)
- D = Diffusion constant for the sampled compound (cm²/min)
- c = Concentration of the measured substance in air (mg/m³)
- t = Exposure time (min)
- A = The area of the exposed filter (cm²)
- L = The distance between the filter and the lid of the sampler (cm)

1.1.3 The GMD- sampler

The GMD-sampler consists of 4 parts (fig.2). A badge housing, a coated filter, a screen and a sliding cover [6]. The screen is divided into two parts, one with holes and one without. To start the measuring the sliding cover is moved to the other side so that the part of the screen with the holes becomes visible. To stop the measuring the sliding cover is replaced and the time the sampler has been open is noted. After closing the filter is analysed and the air level is calculated with the formula above.



Figure 2: The GMD sampler with an exposed filter.

1.2. Aim

Our aim is to develop a passive sampling method to measure low ozone levels indoors i.e. to find a filter, a solution and an analysis method that suit the needs for a GMD diffusive sampler.

2. Material and methods

2.1. Chemicals

Methanol p.a. (Merck), ethanol 95%, indigo carmine ~85% (Aldrich), glycerol 99,5% (J.T. Baker), toluene p.a (Merck), millipore water, ethandiol (etylenglykol) p.a (J.T. Baker), tetrabutylammonium bromide, TBA 99% (Fluka), dichloromethane 99,5% (J.T. Baker), acetone p.a (Merck).

2.2. Filters

Different types of filters were used and tested; Whatman 41 (\varnothing 185 mm), Whatman silica gel loaded (46 cm x 57 cm), Nitro-cellulose poor size 0,45 μ m (20 cm x 20 cm), Polyamide Sartolon, poor size 0,45 μ m (20 cm x 20 cm), Cellulose acetate, poor size 1,2 μ m (\varnothing 15 cm), Cotton cellulose (25 cm x 20 cm).

Before impregnation the filters were cut into strips with a cutting machine, IDEAL 1058. The cutting machine was cleaned with methanol and paper napkins (Kleenex) so the filters were not contaminated. The strips were cut to fit the diffusive sampler. While cutting and moving the filters (during the whole handling), a pair of tweezers and gloves were used to avoid any touching or defilement.

If the filters were too short for impregnation, the strips were to sew together by hand with patent strong yarn. The strips of Whatman 41, Whatman silica gel loaded, Cotton cellulose, Polyamide Sartolon, Nitro-cellulose and Cellulose acetate were cleaned in methanol for 2 minutes. Filters of Cotton cellulose were cleaned first with toluene, then with methanol. The cleaned filters were hanged up to dry vertically in a fume cupboard.

Some of the Whatman 41 strips have also been cut to a size that matches the diffusive sampler (2,1 x 4,3 cm). These were dipped into methanol and dried in an exicator with an air current led through it.

The Cotton cellulose, Polyamide, Cellulose acetate and Silica gel loaded filters were examined in a microscope.

2.3. Solution of indigo carmine

2.3.1. Solution 1

0.80 g indigo carmine was solved in 50 mL methanol and 0,5 mL glycerol. A magnetic stirrer was used to make the solution homogeneous [3].

2.3.2. Solution 2

0.80 g indigo carmine was solved in 300 mL methanol and stirred for 5 minutes. 700 mL methanol and 5 mL glycerol was added, followed by ultrasonical mixing for 10 minutes.

2.3.3. Solution 3

4.0 g indigo carmine was solved in 400 mL millipore water and stirred for 5 minutes. 600 mL methanol and 5 mL glycerol were added, followed by ultrasonical mixing for 10 minutes.

2.3.4. Solution 4

4.0 g indigo carmine was solved in 1L millipore water and stirred for 5 minutes. 10 mL glycerol was added and the solution was ultrasonically mixed for 5 minutes.

2.3.5. Solution 5

30.0 mg of indigo carmine was solved in 15 mL ultrapure water; 15 mL of ethandiol was added, followed by ultrasonical mixing for about half a minute. Finally the water/glycerol mixture was diluted to 100.0 mL in acetone and mixed again shortly [3].

2.3.6. Solution 6

A) 100.0 mg indigo carmine was solved in 10 mL Millipore water. B) 140.0 mg TBA was solved in 10 mL Millipore water. 1 mL of solution A was mixed with 3 mL dichloromethane (the solution is now in two phases) and 1 ml of solution B was added. The solution was shaken for 15 minutes. The lower phase (dichloromethane) was moved into a test tube (1). This procedure was repeated. 3 mL dichloromethane and 1mL of solution B were added to the indigo carmine solution. This solution was shaken for 15 minutes. The lower phase was moved to the test tube (1).

2.4. Impregnation

2.4.1. Method 1

The filters (Whatman 41) that were already cut into the right size (2,1x 4,3 cm) were dipped into the indigo carmine solution number 1, and were placed in an exicator to dry with a current of ozone free air through it.

2.4.2. Method 2

A cylinder box made of Teflon was used to impregnate some of the filters. The box had a lid and 3 glass rods placed above one of the sides to remove any surplus of solution (fig 3a). The filter strip was put into the solution for 5 minutes (Cotton cellulose in solution 2) or 10 minutes (polyamide and cellulose acetate in solution 3 and cotton cellulose in solution 4). Then it was pulled around the sticks with a regular speed and angle with a pair of tweezers (fig 3b).

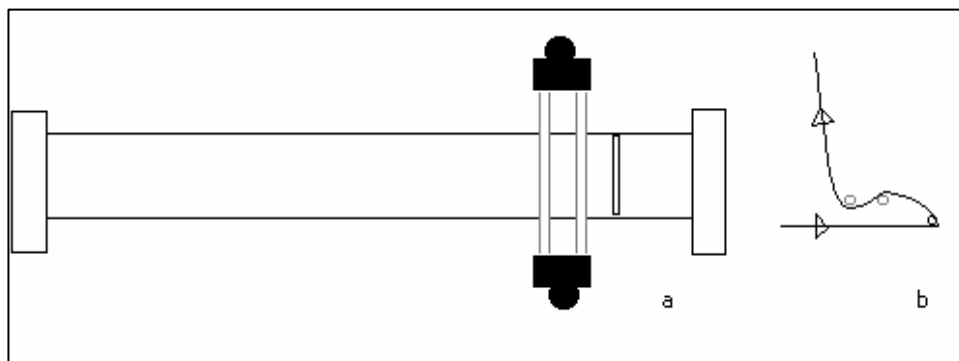


Figure 3a The box made of Teflon seen from above.

Figure 3b The filters are pulled around the glass rods as the picture shows.

2.4.3. Method 3

Strips made of silica loaded filters were impregnated (solution 5 and 6) with a microinjection pump (CMA/100 CMA/Microanalysis) and a printer (2210 Recorder 1 channel LKB Bromma). The printer pulls the filter at a regular speed (the filter is fastened to the roller) under the syringe (Micro Syringe of 5 ml) that drips with a specific flow. When using Solution 5 the filter speed was 2,5 cm/min and the flow of 200 μ l /min. When using Solution 6, the printer had a speed of 2,5 cm/min and the flow was 250 μ l /min. Glass rods were placed between the Microinjection pump and the printer to keep the filter horizontal. (Figure 4)

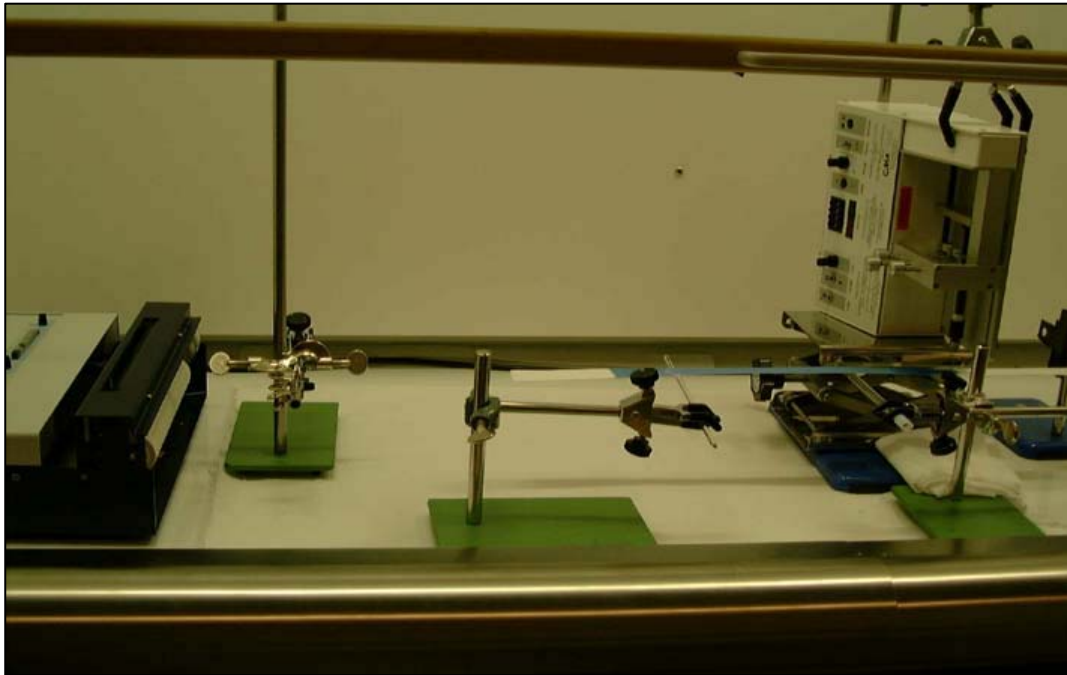


Figure 4: Coating with microinjection pump.

2.3.4. Drying

After impregnation the filters were put into a plastic box with a cover to dry. The strips were hung horizontal and the box had a constant nitrogen flow led into it (0,5 l/min). The filters were kept in the box until the loading of the diffusive sampler.

2.4. Mounting of GMD Sampler

The filter strips were cut into the right size (2,1 cm x 4,3 cm) with the cutting machine. Before cutting the machine was cleaned with methanol and paper napkins (Kleenex). A sheet of writing paper was placed over the filter so it would not contact the cutting machine's manual clamp. While cutting, a pair of tweezers was used.

After cutting the filter was mounted in the diffusive sampler with a pair of tweezers. The samplers were kept in aluminium bags along with unexposed impregnated filters (1/aluminium bag) and put into the freezer. The unexposed filters protect the mounted samplers from ozone in the air.

2.5. Ozone exposure

To expose the samplers for ozone, a Teflon box was used, 8,1 cm x 6,2 cm x 90,2 cm (fig 5). The box had 4 doors and 7 ventilators. The ozone was measured from the 4th ventilator by an ozone measure instrument (ML 98 11). Ozone from an ozone generator (500 MM Fisher Technology) was led into the box and the ozone passed a plate of Teflon continuously to bring an even flow over the GMD samplers, which was placed as shown in figure 5 [5].

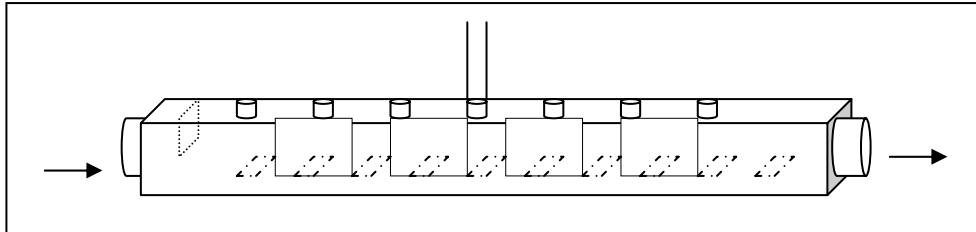


Figure 5: Exposition chamber.

The exposition level of ozone was 500 μg and the exposition time 1 –5 hours. GMD Sampler was opened before placing it in the box and closed directly after exposure.

2.6. Analysis

2.6.1. High Performance Liquid Chromatography

Exposed samplers from method 1 were analysed by HPLC 1100 manufactured by Hewlett Packard (Zorbax SB-CN 2,1 mm x 15 cm PN 883700.905) [7]. After exposure, the filter was cut in two pieces, one exposed and one blank. The pieces were put in test tubes with 5 mL millipor water each and these were put in an ultrasonical bath for 10 minutes.

2.6.2. Near Infrared Spectroscopy

Exposed samplers from method 2 and 3 were analysed with NIR [8]. The NIR instrument used was a NIR-Systems SY-1256 Versatile feed and forage analyser (FOSS NIRSystems Inc., Silver Spring, MD) with a model 5000 monochromator. The instrument measures 700 wavelengths in the interval 1100-2500 nm. Internal standard of aluminium was used. Diffuse reflectance (R) was recorded, and transformed into apparent absorbance (A) according to $A = \log(1/R)$.

3. Results and discussion

3.1. The choice of filters

Filters made of nitro-cellulose were damaged in contact with methanol and therefore excluded.

The cotton cellulose filter has small fibres and there is no noticeable difference between the two sides. The polyamide filter has an even surface and the cellulose acetate filter is fibrous and sensitive of touch. The silica-loaded filter has small fibres and a check pattern on one side. The check pattern is placed downwards while impregnating the strips and mounting the diffusive sampler.

The filter that eventually was chosen as the best filter while impregnating and touching (it was less sensitive for tweezers and solutions) was Whatman silica gel loaded (46 cm x 57 cm).

3.2. Solution of indigo carmine, impregnation and analyses

While impregnating (method 1 and solution1) filters (Whatman 41) precipitation of indigo carmine was discovered in the solution and after drying the filter had an obvious colour unevenness.

It is not possible to make a solution of indigo carmine according to Grosjean and Hisham [3] . Therefore, this solution (1) was excluded. Method (1) made uneven results on the filters and was also excluded.

Using method 2 it was difficult to pull the filters at an even speed. Solution 2 and 3 precipitated and solution 4 made the filters dry slowly. The polyamide filters became wrinkled after cleaning and impregnation and the cotton cellulose and cellulose acetate filters were spotted after impregnation.

In the NIR- analysis it was not possible to find any correlation between the amount ozone reacted on the sampler and the NIR-adsorption due to the uneven impregnation. These filters, solutions and method described above were therefor excluded.

While using method 3 we found the right speed and type of solution while impregnating with solution 6. The filters from solution 5 were not analysed due to uneven impregnation. It was difficult to keep the filters right below the syringe and perpendicular to the syringe. This method resulted in even impregnated filters (when looking at tit with the eyes) and these filters were also analysed with NIR.

3.3. Analysis by High Performance Liquid Chromatography

When using HPLC-analysis the amounts of unreacted indigo carmine were determined on both the unexposed and the exposed part of the filter. The amount of ozone was calculated from the difference of these determinations. Due to the uneven impregnation of indigo carmine on the filter it was not possible to use this analysis method. One result is shown in fig 6.

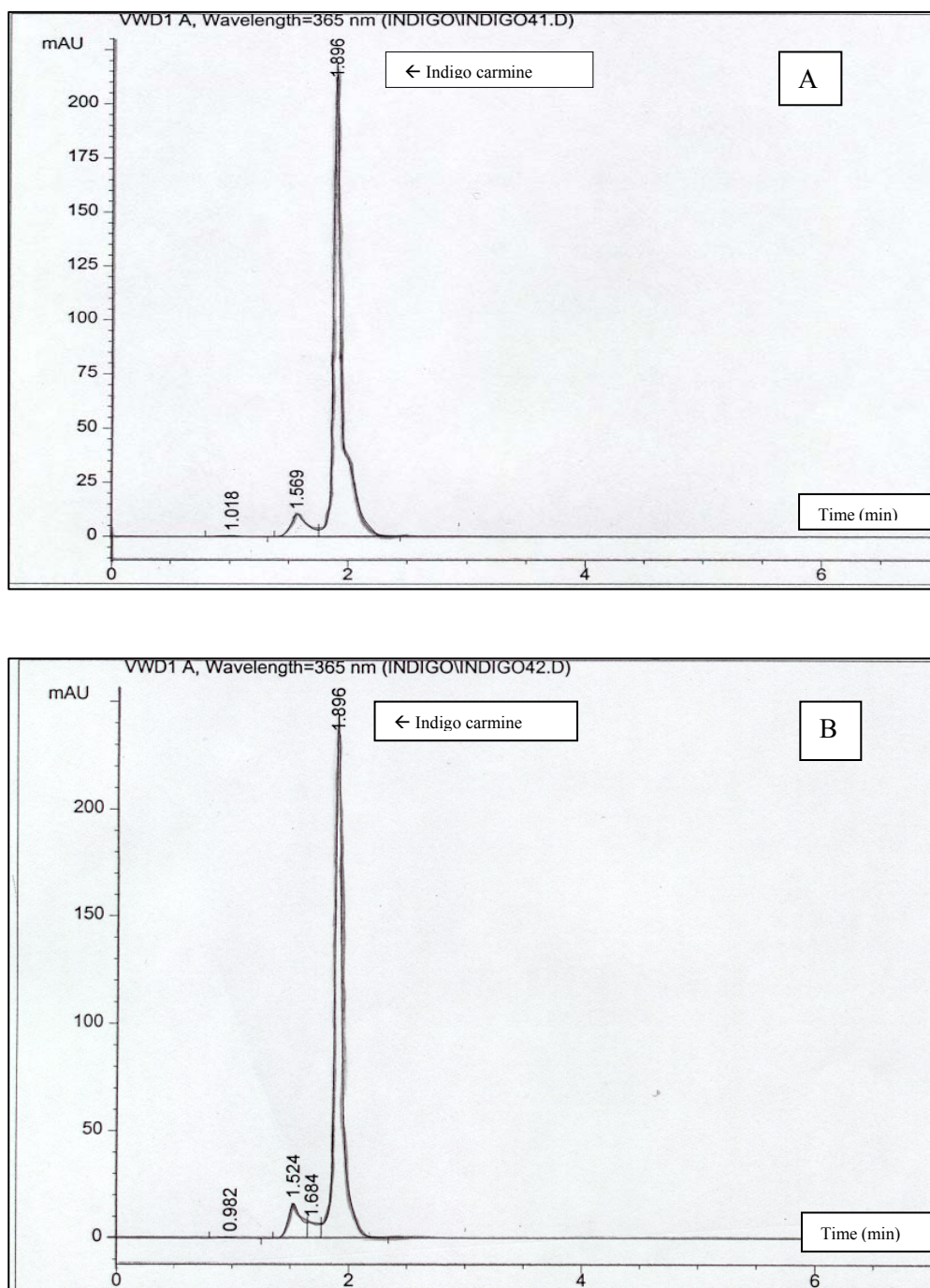


Figure 6. Chromatograms from filters with an uneven impregnation of indigo carmine. Indigo carmine in A has the same height as indigo carmine in B.

3.4 Analysis by Near Infrared Spectroscopy

In the NIR-analysis the samples are exposed to electromagnetic radiation which causes vibration of the hydrogen atoms in the molecule. The energy uptake is measured as absorbance. The wavelengths interval was 1100-2500 nm and the instrument measured at 700 wavelength in this interval which means that a great amount of data are produced for each measure of sample. It is therefore necessary to treat data with a multivariate statistic method, Partial Least Squares Projection to Latent Structures, PLS [9]. A recorded spectra is the sum of spectra from indigo carmine and the reaction products.

The great advantage of NIR-analysis is that solid sample, the impregnated filter, is mounted in the probe and analysed directly without any further treatment.

The NIR analysis of the prepared samples (silica gel filters, solution 6 and method 3) are presented in figure 6. For each sampler both the exposed and the unexposed filter are analysed and the difference between the results are calculated. Three samplers are exposed at each time in the exposition chamber and the mean of these samples are calculated. The results in figure 6 show a correlation between the amount ozone/exposition time and the absorbance. It is similar to a calibration curve. Thus, the use of NIR analysis to determine ozone amounts in the filter showed to be very suitable.

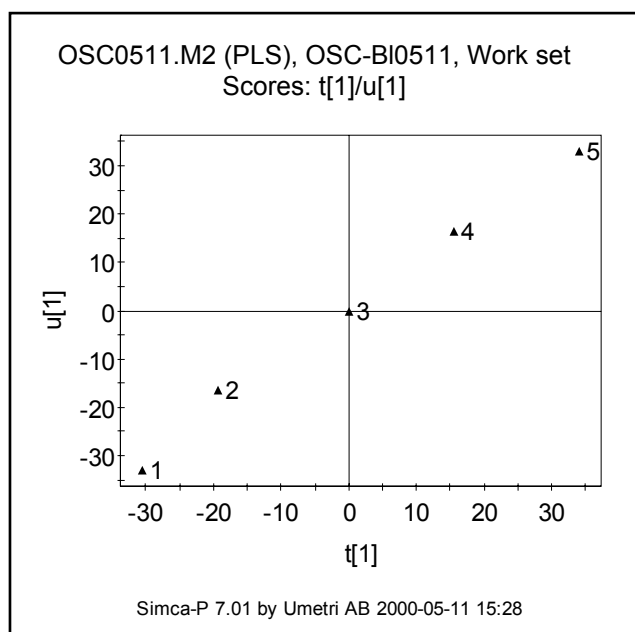


Figure 7. PLS analysis of data from the NIR-analysis of the samplers (the mean of three samplers at each exposition time 1, 2, 3, 4 and 5 hours)

4. Conclusion

While trying to develop this diffusive sampler we found that the best filters were Whatman silica gel loaded impregnated with solution 6, using method 2. NIR was also found to be the best analysis instrument.

These results are well approved as the results we searched for while formulating our aim, but it is always of great importance to discuss the importance of the work. One should always be aware of the fact that we have used many technical instruments and that there could exist both calibration and reading mistakes. To be absolutely sure about our results concerning type of filter and solution, it might be necessary to examine these factors sensibility and possible effects of humidity or varying wind speed. The experiments should also be tested more times before it can be established whether these results are the ones to be used in future.

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