Exam in Methods for Environmental Monitoring, FKFN35
Tuesday August 20 2019, 8:00-13:00, IKDC, room 402
Use a separate sheet of paper for each question. Note the number of papers handed in on the cover and mark which questions you have tried to answer.
Answer the questions in English or Swedish.
You may very well use figures/drawings or tables/lists in your answers.

Back pack, telephone and books, etc. at the coat hangers, and not by your desk.

To pass, minimum 50 % on the written exam.

Total points: 54p (50 % = 27p).

1. Biomarkers (6p)

Workers are worried about inadequate protection from styrene exposure in a factory producing styrene from ethylbenzene (see Figure 1). Mandelic acid is a metabolite of styrene with a biological half-life of 5.3 ± 1.1 hours. Mandelic acid is analysed with LC-UV.
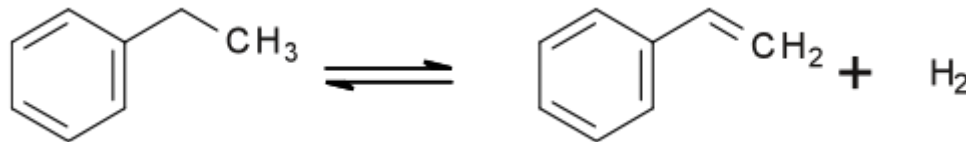

Figure 1. Ethylbenzene is mixed in the gas phase with 10–15 times its volume in high-temperature steam, and passed over a solid catalyst bed made of iron(III) oxide.

  a) Choose a suitable biological matrix and explain why you choose it and when to take biological samples in about two sentences (2 p)
  b) What reservation could be expressed about Mandelic acid suitability as a monitored metabolite and what methodological demands could possibly not be fulfilled? (2 p)
  c) Motivate whether the analytical method require the addition of a deuterium labelled internal standard to the samples prior to analysis with LC-UV? (2 p)

Answers:

  a) *Slide 42-45, Urine has the most suitable half-life and are none invasive, after work-day*
  b) *Slide 72, Ethylbenzene also produce mandelic acid (phenylglyoxylic acid is more specific). Not Metabolic or Source specific.*
  c) *Slide 85, UV-detection analysis specific light reflection/absorption/fluorescence and not mass ratio.*

2. Optical techniques (10p)

(a) Draw a half polar plot and mark the scatter angles from 0° to 180°. The light impinges on the sample from left to right, add an arrow indicating the incidence of light. Add the following techniques in the correct place in the plot:

        * Lidar
        * Nadir satellite imaging
        * TDLAS (Tunable Diode Laser Absorption Spectroscopy) (3p)

(b) When light impinges on a sample such as the atmosphere, the ocean or snow, which optical properties affects the mean penetration depth and how? (2p)

(c) The surface temperature of the Sun is 5770 K and its peak emission wavelength is in the green region at 502 nm. Calculate the peak emission wavelength from Earth at room temperature and spell out the corresponding region in the electromagnetic spectrum. (2p)

(d) Draw a spectrum of vegetation and add wavelength numbers. Elaborate on prominent spectral features governing the spectral signature from vegetation. (3p)

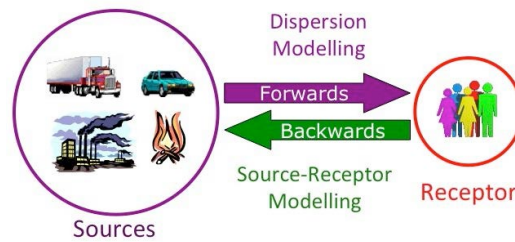## 3. Dispersion and source/receptor modelling (10p)

Figure 2. Only included as illustration.

(a) Describe which two types of input data area crucial for dispersion models and how they are used in the model with a few sentences (Hint: not measurements). How can you calculate the air pollution concentrations with a dispersion model? (3p)

(b) Explain the principles of source/receptor models. Explain it by including a description of the data matrix, source profiles, and source contributions. No equations and explanation of difference between chemical mass balance and factor analytical models needed although you might use equations to explain your answer if you want to. Hint: You can use Figure 3 below for your explanation if you find it useful. (3p)

(c) Figure 3 shows hypothetical measurement data (no units shown in the figure) from a town in northern Sweden with a lot of residential wood combustion. During especially cold days, the air quality is severely affected by wood combustion. Also, traffic exhaust from personal cars affect the air quality to a large extent. Please explain the difference between chemical mass balance source receptor models and multivariate factor analytical source receptor models with Figure 3 as example and how these models can recognize how much traffic and wood combustion contribute to the air pollution in the town. (4p)

Time	K (aerosol)	Benzene	Toluene
2010-01-07	0	3	6.5
2010-01-08	0.2	2.2	3
2010-01-09	1	3	1
2010-01-10	And so on..	...	...

	Cars	Wood
K	0	2
Benzene	3	6
Toluene	7	2

Figure 3. Measurement data (left panel) of potassium in aerosol particles (K), and gaseous benzene and toluene from diurnal samples in January 2010 in a northern Swedish town affected by wood combustion and car traffic exhaust. The right panel shows a source profile used for source receptor modelling in the town.

Answers:

a) Emission data (emission database, how much each source emits), and meteorological data (how are the winds and other meteorological factors spreading out the pollutants). (2p) The emission at one point taken from the emission database is spread out like a chimney plume to the surroundings using the information from meteorology. The model is discrete, meaning pollution from one time and one box is transported in a small time phrame to the other surrounding boxes. (3p)

b) S/R modelling relies on the principle that measured concentrations (one part of the data matrix) during one time instance can always be represented as the product of the source

profile and the source contribution with all sources added together. A source profile is basically the relative emissions of different compounds from a specific source, which are used in the S/R model. The source contribution is the relative (or with more advanced models, the absolute) contribution to the measured concentration of a compound from the different sources, which influence the compound. Source contribution can be retrieved from each time instance. For each time instance, the model is looking at how relative concentrations of measured compounds "look like" compared to source profiles, and decides how each source profile adds up to the total measured concentration, which is the source contribution. This doesn't give extra points: "Some models take into consideration larger uncertainties in measured compound concentrations, and put less effort into matching this specific compound, and puts more weight into identifying the correct sources for the other compounds." (3p)

c) Chemical mass balance models rely on a known source profile like in Figure 3. The only unknown is the source contribution, which can be calculated from the known two sources and using the source profile as input data. The known source profile does not allow for the model to interpret the source contribution in its own way. Rather, it tries to apportion for example 7 January entirely to car traffic exhaust, and January 9 entirely to Wood combustion, since these days match almost perfectly with each of these source profiles. Converesly, in a factor analytical model, the source receptor model tries to estimate the source profiles on its own, and the number of sources can vary. Hence you do not use the source profile as input, you get it as output. Note: Likely, the multivariate source profile model outcome with two chosen sources from Figure 3 will be similar to the source profile in Figure 3, since these data are relatively clear and matches the source profile in Figure 3. (4p)

4. Nuclear microprobe analysis (12p)

PIXE

(a) What are characteristic X-rays and how are they created in PIXE? (1p)

(b) Explain the major <u>advantage</u> of PIXE over EDX as used in modern electron microscopes? (1p)

(c) What are some <u>dis</u>advantages of PIXE compared to EDX as used in electron microscopes? Give two. (1p)

(d) Can PIXE by used for isotopic analysis and how/why? (1p)

(e) PIXE is stated to be an absolutely quantitative technique. What does it mean? (2p)

14C analysis

^{14}C is a versatile tracer used in several disciplines such as environmental science, climate research, archaeology and geology.

(f) What two types of measurement techniques can be used for detection of ^{14}C? (1p)
(g) Describe the general physical principles of each of the detection methods. (4 p)
(h) Which of the two techniques is more suitable for aerosol source apportionment, and why? (1 p)

Answers:

(a) X-rays emitted when outer-shell electrons fill a vacancy in the inner shell of an atom, in PIXE the vacancies are created by high energy (MeV) protons.

(b) The higher mass of the proton gives a much lower background from Bremsstrahlung and reduces the detection limits by a factor of 1000.

(c) PIXE requires much larger equipment (can take up a whole laboratory), PIXE needs an experienced person(s) to operate the equipment, PIXE is much more expensive.

(d) No, the characteristic X-rays measured are not influenced by the number of neutrons in the nucleus.

(e) Having a calibrated system; detector solid angles, absorbers, distances known – all

(f) Decay counting (e.g. proportional counting or liquid scintillation counting) (0.5 p); Accelerator mass spectrometry (0.5 p)

(g) *Decay counting (one of these should be mentioned): (1 p)
1. Proportional counting: The sample (about 1 g) is combusted to CO2 and the decay of 14C is measured in a gas proportional counter, usually for several days
2. Liquid scintillation counting: the 14C is somehow trapped in a liquid and mixed with a scintillation cocktail: the decay is registered.

*Accelerator mass spectrometry (AMS) (3 p): Carbon (size: mg) in sample is extracted to graphite which is pressed into a sample holder and placed in an ion source. Negative carbon ions are extracted in a Cs sputtering source (12C-, 13C-, 14C-). Apart from 14C-, also molecules are extracted with almost equal mass as 14C-, eg. 13CH-: these need to be removed prior to detection. The basic steps are: ion production in ion source, energy analysis in an electrostatic analyser, mass slelction in a low-energy dipole magnet, acceleration to 240 keV, stripping (which breaks up molecules and shift the ion beam from negative to positive: this required high energy of the ions), mass, energy and charge

selection in magnetic field, final analysis in electrostatic analyser. The system switches between the different carbon isotopes to get the percentage 14C in the sample. The measurement is done relative to standard of known activity and 14C-tree blanks.

(h) Only AMS because of the small sample sizes. (1 p)

5. Sampling strategy (6p)

You work in an environmental department of a municipality in Sweden, and you would like to measure how large is the pollution coming from a typical, relatively trafficked highway in the outskirts of your town.

(a) What kind of measurement strategy would you employ to find out how much the highway is polluting downwind of the highway, and how do you subtract for the influence from background pollution (long range transport)? (3p)

(b) What three different health relevant pollutants (one gaseous and two particle properties) would you measure to deduce the effect on air quality and human health? (3p)

Answers:

(a) Measure downwind of the highway. If we have prevailing winds from the west in Sweden, it is clever to measure east of the road (concentration east point). By measuring also to the west of the highway (concentration west point) when we have winds form the west, we get the background contribution. Then we get traffic influence as: concentration east point subtracted by concentration west point. (3p)

(b) From car traffic you have health relevant parameters, particles: Road dust particles, soot diesel particles, organic carbon particles, PAH particles, metal particles, and so on. Gaseous: NOX, different organic gases, toluene, xylene, benso(a)pyrene, and so on. However, emissions of toluene, xylene and benso(a)pyrene are not very high.

Ozone and CO_2 don't give correct answers, since the first one is not a pollutant, and the second one is formed further downwind of the highway after chemical reactions with NOX, and not close to the highway. SO_2 and lead are not correct either. Car traffic in Sweden have very small emissions of SO_2 and lead nowadays.

6. Aerosol particle and gaseous measurement techniques (10p)

(a) Describe the basic principle of two different aerosol particle measurement techniques with a few sentences. State if these are reference methods, equivalent as reference methods for air quality standards, or if they are non-reference methods (3p) Note: You get 2p for describing the techniques and 1p for stating their status as reference method, equivalent method or neither. It is not allowed to describe a technique, which you have already been describing in one of the other questions.

(b) Describe the basic principle of two different gaseous measurement techniques with a few sentences. State if these are reference methods, equivalent as reference methods for air quality standards, or if they are non-reference methods (3p) Note: You get 2p for describing the techniques and 1p for stating their status as reference method, equivalent method or neither. It is not allowed to describe a technique, which you have already been describing in one of the other questions.

Figure 4 shows the size resolved chemical composition of the particle ensemble measured at the regional background site at Söderåsen using Aerosol Mass Spectrometry. Total organic, and the three inorganic components nitrate (NO_3^-), sulfate (SO_4^{-2}) and ammonium (NH_4^+) are shown. The y-axis shows particle mass concentration, the x-axis shows particle diameter calculated from Particle-Time-of-Flight. The data is averaged over two months, and contains signal from approximately 20 million particles. Motivate your answers, or explain why the figure cannot be used to answer the following questions:
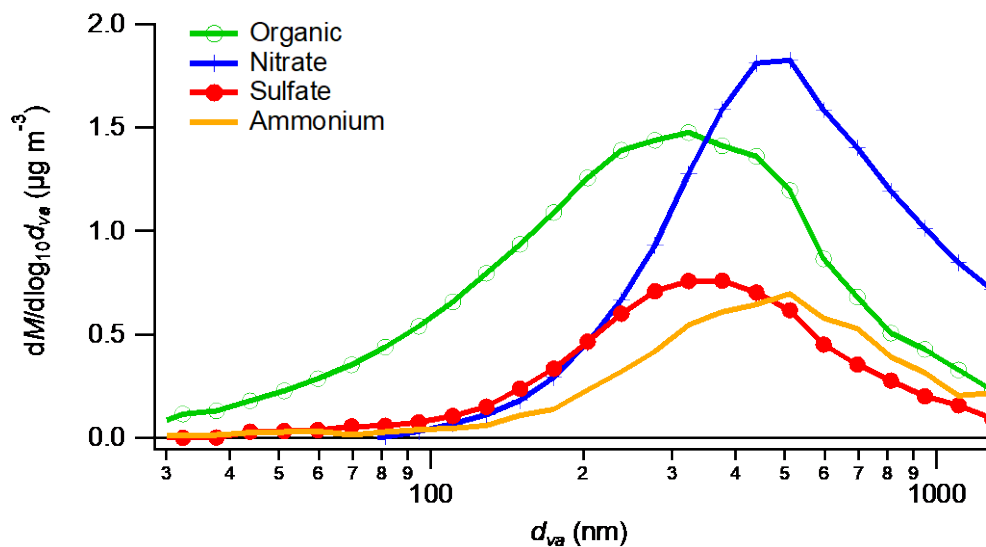

Figure 4. Size resolved chemical composition of fine particles in the regional background aerosol.

c) Describe the mass average chemical composition between dva 30 nm and 50 nm. (1p)

d) In what size range can one expect particles with the highest mass fractions of nitrate ? (1p)

e) Did most of the particles contain >10% sulfate? (1p)

f) A mischievous demon has retroactively replaced all the nitrogen atoms sampled by the instrument with N_{15}. (N_{15} refers to nitrogen with atomic mass 15 amu. N_{14} dominates nitrogen under normal circumstances). How will this change the mass spectrum shown in Figure 5 below? (1p)
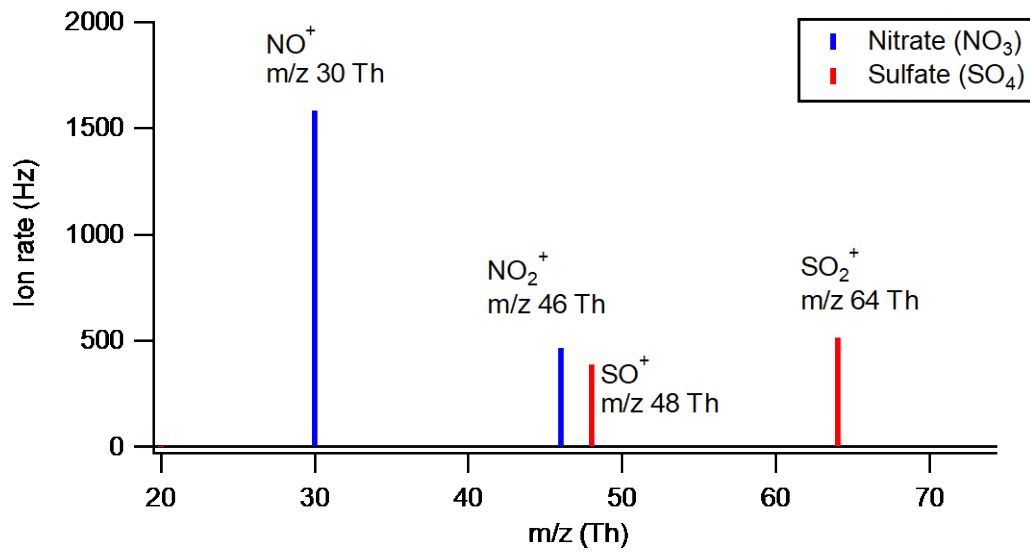
Figure 5. Example of mass spectrum recorded at Söderåsen, Scania, Sweden.