Chromatographic non-CO_2 gases measurements at Kasprowy Wierch station

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- Introduction and motivation

Atmospheric Station Kresin u Pacova is located in Czech-Moravian Highlands (535 m a.m.s.l) close to Observatory Košetice (CHMI). Beside the monitoring of greenhouse gases (CO_2, CH_4, N_2O) there is provided a monitoring of O_3 and Hg in vertical profile. Spectroscopic methods are used for continual sample analysis. Monitoring of Rn, isotopic composition of atmospheric CO_2 and vertical profile of aerosols are planned or prepared.

Kasprowy Wierch station is located on the mountain peak (1987 m a.m.s.l) in High Tatra in Southern Poland. It has been monitoring air composition since 1996, mainly with the use of gas chromatography technique. Advanced sampling program is also continued for monitoring of isotopic composition of atmospheric carbon dioxide.

At both monitoring station measurement program goes parallel and comparison of measurement strategy, sampling techniques, data mining routines will help in solution of forthcoming technical and engineering problems.

- Scientific objectives

A presentation and introduction to the gas chromatography techniques used at the Kasprowy Wierch site with the detailed description of the equipment configuration and QC/QA procedures.

Collection of a series of glass flasks at Kasprowy Wierch site during different times of the day and subsequent analysis with gas chromatograph and comparison with direct continuous measurement

Determination of mixing ratios of methane and nitrous oxide and related species at the site.

Reanalysis of the archive dataset from Kasprowy Wierch station with a careful study of impact of the calibration strategy on quality of the data.

Estimation of measurement uncertainty with different statistical approach

- Reason for choosing station

The Observatory Kasprowy Wierch was chosen to visit because there are used mainly sampling methods that are currently being prepared for use in AS Křešín, possibly on their introduction to future consideration. The reason was even possible cooperation in the preparation of calibration gases and also geographic proximity advantageous for possible future cooperation.

- Method and experimental set-up

Atmospheric mixing ratios of CO_2 and CH4 are measured using automatic gas chromatographs Hewlet Packard 5890 (at Kasprowy Wierch) and Agilent 6890N (in Krakow). Instrumens are equipped with a flame ionization detector (FID), a 3 m column (Porapak QS) and nickel catalyst converting carbon dioxide to methane. Nitrous oxide is measured using an electron capture detector (ECD) and double-column system configured in a back-flush mode(2 m pre-column Hysep Q 80/100 and 4 m analyticalcolumn Hysep Q 80/100). This analytical set-up allows the measure ment of CO_2, CH_4, and N_2O in a quasi-continuous mode, with consecutive measurements performed ev ery 15–30 minutes.

- Preliminary results and conclusions

A familiarization with the methods and equipment used in the workplace AGH-UST in Krakow and directly in the Observatory Kasprowy Wierch was as a part of the visit. Options of continual and semicontinual determination of GHG with chromatographic and optical methods were discussed. Since the AS Křešín Pacova is equipped with continuous IR analyzer for determining CO_2, CH_4 (Picarro), CO and N_2O (LGR), we focussed especially to possibility of semicontinual determination of SF6 and halogenated hydrocarbons with gas chromathoraphy. Possibility of using a cryogenic preconcentration for halogenated compounds was discussed including a demonstration of a custom-build cryo-preconcentration unit

Familiarization with the methodologies used and equipment including remote management and maintenance was held. Also originally unplanned familiar with maintenance and servicing was was done in the context of practical exercises at the observatory Kasprowy Wierch during repairing a fault on the system of dosing valves of the sampler.Full calibration procedure by a set of primary standards was performed in the framework of service intervention.

A series of glass flasks at Kasprowy Wierch site during different times of the day and diferent meteorological condition was collected in the frame of practical exercise and subsequently analyzed with gas chromatograph. An effort was put on drying procedure and its influence on measurement results was discussed. Due to the failure of the sampler in the Observatory Kasprowy Wierch a subsequent comparison with direct continuous measurements was not done. Samples for determination of halogenated compounds were collected in the night during strong inverse meteorological situation when the station was sampling free troposphere.

For reasons of time caused by delays in servicing in the observatory reanalysis of the archive dataset and estimation of measurement uncertainty with different statistical approach were not realized. Impact of integration parameters, methods of interpolation and nonlinearity estimation were only tested on the small sample of data in the frame of practical exercise.

- Outcome and future studies

Information and experience obtained during a visit to the Observatory Kasprowy Wierch will be used during the gradual equipping of the Atmospheric Station at Křešín u Pacova so that its potential can be maximally exploit. This applies in particular to the possibility of direct semicontinuous determination of SF_6 and halocarbons with the gas chromatography method. In particular, operational experience and practical verification of claims of equipment operating in automatic mode, remote administration (GC) appears to be very valuable in finding technical solutions suitable for Atmospheric Station Křešín u Pacova.