Atmos. Meas. Tech. Discuss., 2, C371–C373, 2009
www.atmos-meas-tech-discuss.net/2/C371/2009/

Atmospheric Measurement Techniques Discussions

Interactive comment on "A single gas chromatograph for accurate atmospheric mixing ratio measurements of CO_2, CH_4, N_2O, SF_6 and CO" *by* S. van der Laan et al.

Anonymous Referee #2

Received and published: 11 July 2009

General comments: The manuscript gives a clear and comprehensive description on a new gas chromatographic method that allows the determination of five compounds using two detectors where other currently established analytical methods are in need of a third detector. This method is a significant advancement of similar systems used at other locations. However, the manuscript does not make as clear which parts of the method are constituting a progress and which parts are established chromatographic procedures that are already used by many labs. The described method is based on common gas chromatographic procedures for greenhouse gas analysis that have been described previously (e.g. Worthy, Measurement Procedures and Data Quality. In: Canadian Baseline Program; Summary of progress to 2002, Meteorological Service

of Canada, Chapter 4, pages 97-120, 2003; Ramonet et al, The French Trace Gas Monitoring Program (RAMCES) Report of the eleventh WMO/IAEA meeting of experts on carbon dioxide concentration and related tracer measurement techniques, WMO-GAW No.148, 32-54, 2003; Jordan et al., Continuous GC measurements of trace gases at the Ochsenkopf monitoring station Report of the eleventh WMO/IAEA meeting of experts on carbon dioxide concentration and related tracer measurement techniques, WMO-GAW No.148, 32-54, 2003). There should be some reference to the literature for this. The authors advertise the instrumental method as cost-effective, reliable and "highly suitable for unmanned remote stations". The main economization is the saving of additional instruments for the additional tracer. However, it should be raised that the carrier gas supply at far remote places is costly and that GC maintenance is not done by only providing the gases. Experience at other stations has proven that especially the many valves tend to have a limited life time of months to 1-2 years before needing maintenance and gas generators also may fail.

Specific Comments: In the compilation of methods available in the Introduction section should include the precision quotes for various methods are rather on the poor end: Cavity Ringdown spectroscopy can do far better than 0.2ppm for CO2 and the obtainable precision with the ECD is rather <0.2 ppb than <0.5 ppb for N2O and <0.05 ppt than 0.1 ppt for SF6.

The description of the method is clear and thorough. The approach to check the instrumental response appears not fully adequate: p. 9: The calibrated ranges by the set of higher level calibration t is properly listed. It should be also mentioned which span the Ref high and Ref low cover ("One reference cylinder (Ref.high) contains relatively high mixing ratios, the other one (Ref.low) contains relatively low mixing ratios."). p.11: "Therefore, we can assume that the shape of the response curve does not change significantly over time". It would be preferable if the authors would not need to "assume" but could document this by a record of target gas analysis with different mixing ratio levels ("target high" and "target low") p.15: The system performance appears ex-

cellent for CH4 and good for CO2. In the evaluation of the systems performance it is not appropriate to compare the limited periods of best possible performance with the WMO comparability goals or the total uncertainty of a calibration scale. A disagreement of different international SF6 calibration scales is rather irrelevant for the rating of the quality of the method described. There is a clearly defined WMO scale and as long as other calibration scales have consistent offsets they can be converted to the WMO scale. While it is true that the WMO comparability goal for N2O is more ambitious than what any currently available system provides there are GC systems running with a higher precision than ïĂă0.4 ppb for N2O at monitoring stations (in contrast to "Our obtained precisions are as low as those of the best other measurement systems currently available.")

Technical Comments p.5 should read: All sample loops are flushed for 0.55 (metric) minutes (not seconds) Two small language items to be corrected: p13.: "During this period the period" p14: For a subset of gigure 6, during optimal considtions we find the following “best case” august 2006

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 1321, 2009.