Performance of three INNOVA analyzers for ambient Greenhouse Gas Measurements

Albrecht Neftel
Neftel Research Expertise, Oberwohlenstrasse 27, CH-3033 Wohlen b.Bern, Switzerland
Christoph Flechard
1INRA, Agrocampus Ouest, UMR1069 Sol Agro-hydrosyst`eme Spatialisation, 35042 Rennes, France

Photoacoustic (PAS) trace gas analyzers are based on the principle of light absorbance in a chopped beam that converts the absorbed energy into an acoustic signal that is recorded with a microphone. This technique is reliable and sensitive, but the selectivity depends mainly on the used light source and on the geometry of the absorption cell. E.g. the INNOVA family uses a broadband light source with a selection of suitable wavelength by interference filters.

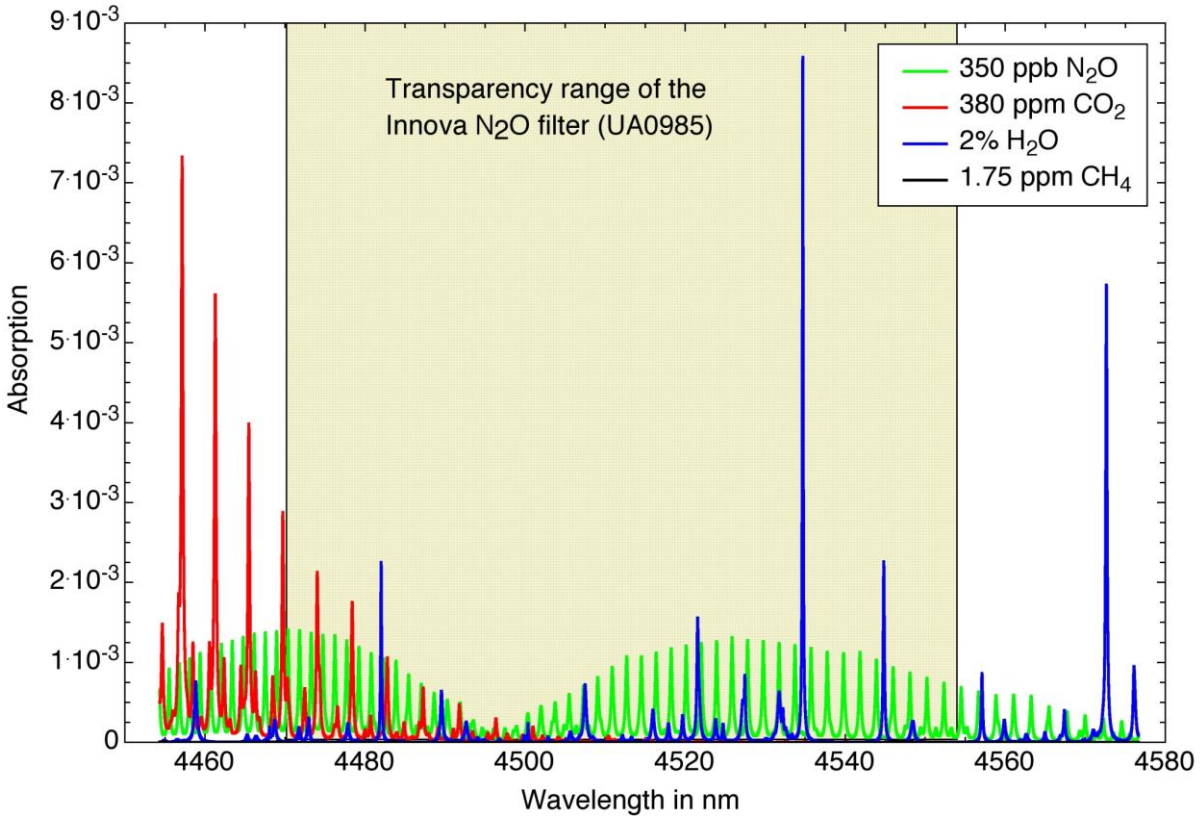

Figure 1: Broadband filters used within the Innova family. As an example, the N_2O transparency window includes absorption bands for CO_2 and H_2O.

In case the absorptions of all trace species in a given window are independent of each other and are strictly proportional to their molecular density (i.e. the amount of absorbing molecules in the light beam) the evaluation of the concentrations needs as many different filters as gases and correspond to the solution of a linear equation systems.

Reality is more complex. Effective absorption coefficients are concentration dependent and are influenced by other absorbing molecules in the window. In addition, the sensitivity of the detection strongly depends on the cell temperature and also on the water concentration.

In 2004 we tested the performance of three INNOVA instruments to measure CO2, N2O, CH4 and H2O in concentration ranges as they typically appear in ambient air in ecosystem research (which, incidentally, are much lower than in the confined air of animal houses). Using the interference correction certified by the manufacturer, the data showed strong deviation for N_2O and CH_4 that systematically depended on water vapor and cell temperature.

Figure 2 shows the effect of varying CO2 and H2O concentrations on the raw signal strength of the N2O filter UA0985 for a N_2O mixing ratio of 300 ppb, ie of the order of the mean atmospheric level . The figure shows that the raw signal varies over one order of magnitude and strongly depends on the cell temperature and water vapour concentration.

N2O raw photoacoustic signal 300 ppb : interference by H2O and CO2

(INNOVA 1312 - N2O filter UA0985)

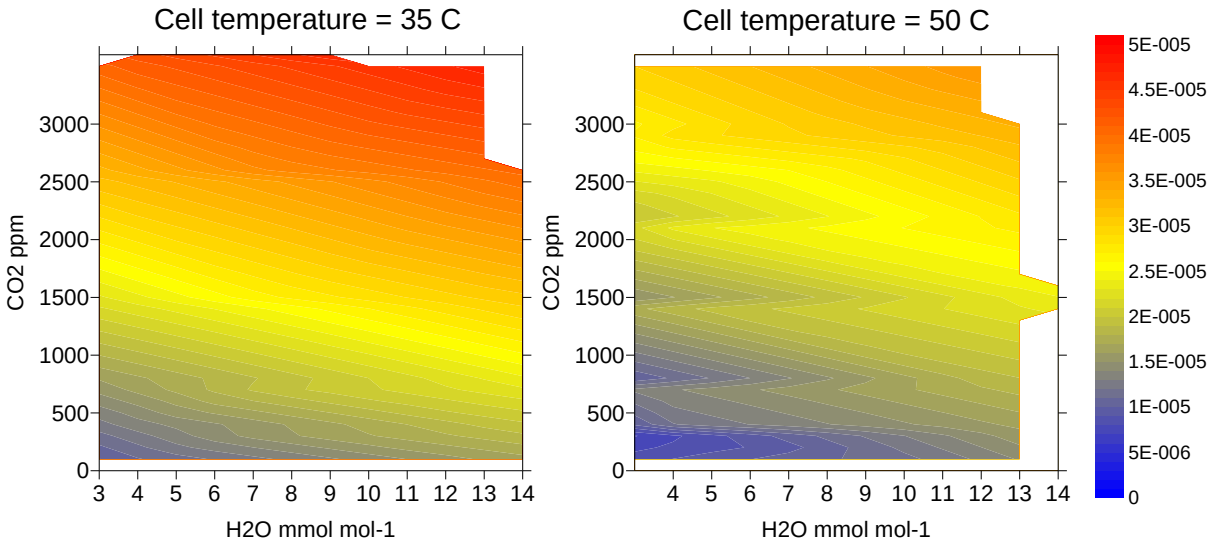

Figure 2 shows the effect of varying CO2 and H2O concentrations on the raw signal strength of the N2O filter UA0985

Figures 3a-c shows the comparison of given standard concentrations and the Innova measurements using the instrument's default correction algorithm for CO2, N2O and CH_4, as function of varying water vapor level and cell temperature.
The data illustrate the strong and systematic deviations from the given concentration, that depends in a complex way from the cell temperature, the water vapor and the level of the other gases. How to read these figures? The experiments are always grouped by four values with fixed CO2, N2O and CH4 concentrations, but increasing cell temperature from 20 to 50°C. These groups demonstrate a very strong influence of the cell temperature. Between the first three groups the N2O concentration changed from 500ppb to 2500ppb and then to 5000ppb. The effect of the N2O concentrations e.g. on the CH4 concentration can then be seen by comparing e.g. always the last point of an individual group over the three groups. Most striking are the strong deviations in the calculated CH4 concentrations that even change the sign and are several times the effective concentration.
Nevertheless, the systematic pattern of the deviations seems to allow to develop a correction algorithm as it was done by Flechard et al. (2005)., but only up to a point: if the ratio of the interfering gas (eg CO_2 or H_2O) to the gas of interest (eg N_2O or CH_4) was too

large, then a very large fraction of the raw signal given by the filter for the gas of interest is actually due to the interfering gas, and the interference can no longer reliably be corrected for due to the large noise in the data.

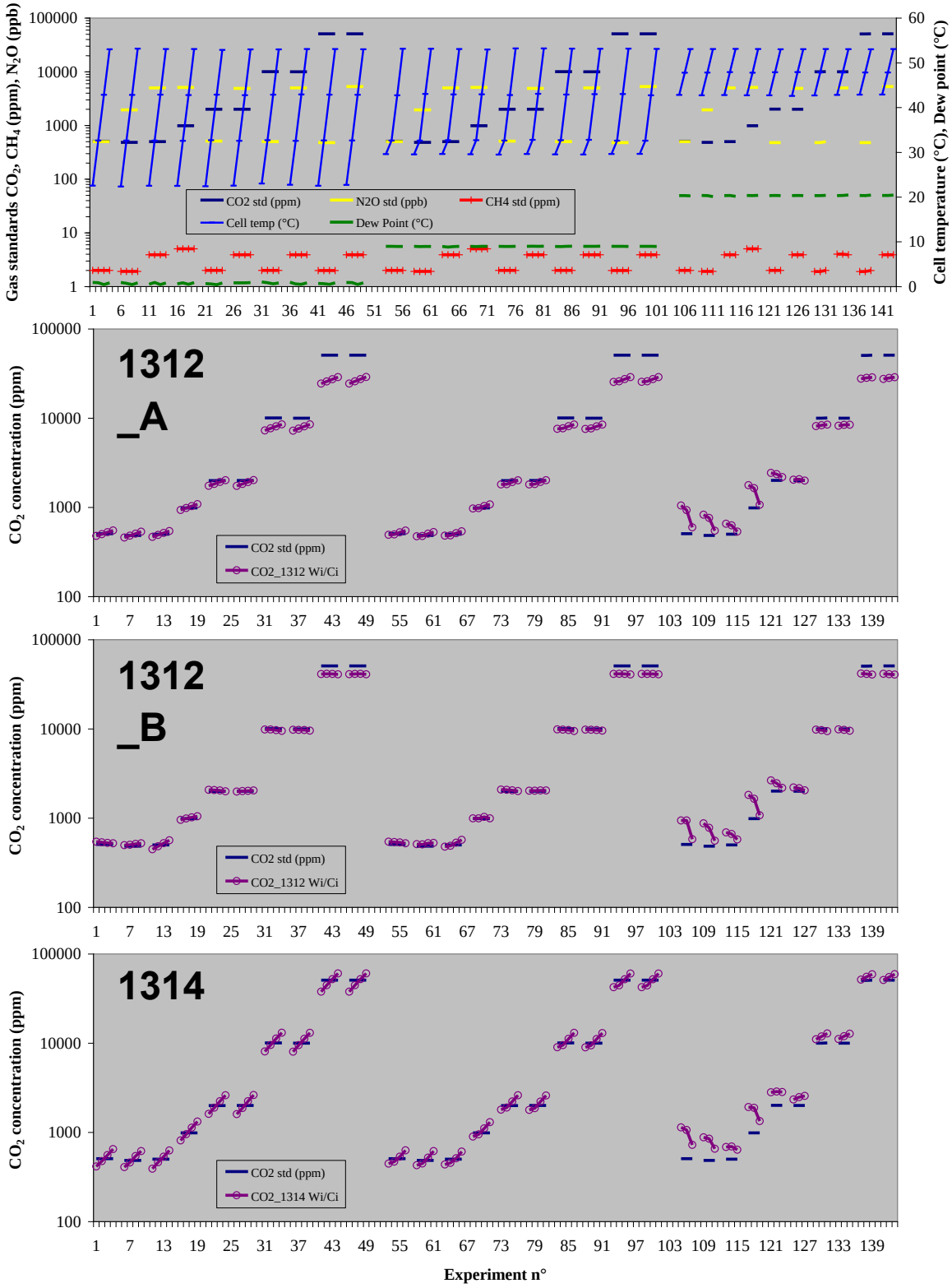

Figure 3a CO2 concentration determined by the Innova's instruments. The number on the x-axis refers to trials with conditions as given in the first panel. The solid lines in the panels indicates the applied standard gas concentration for CO2.

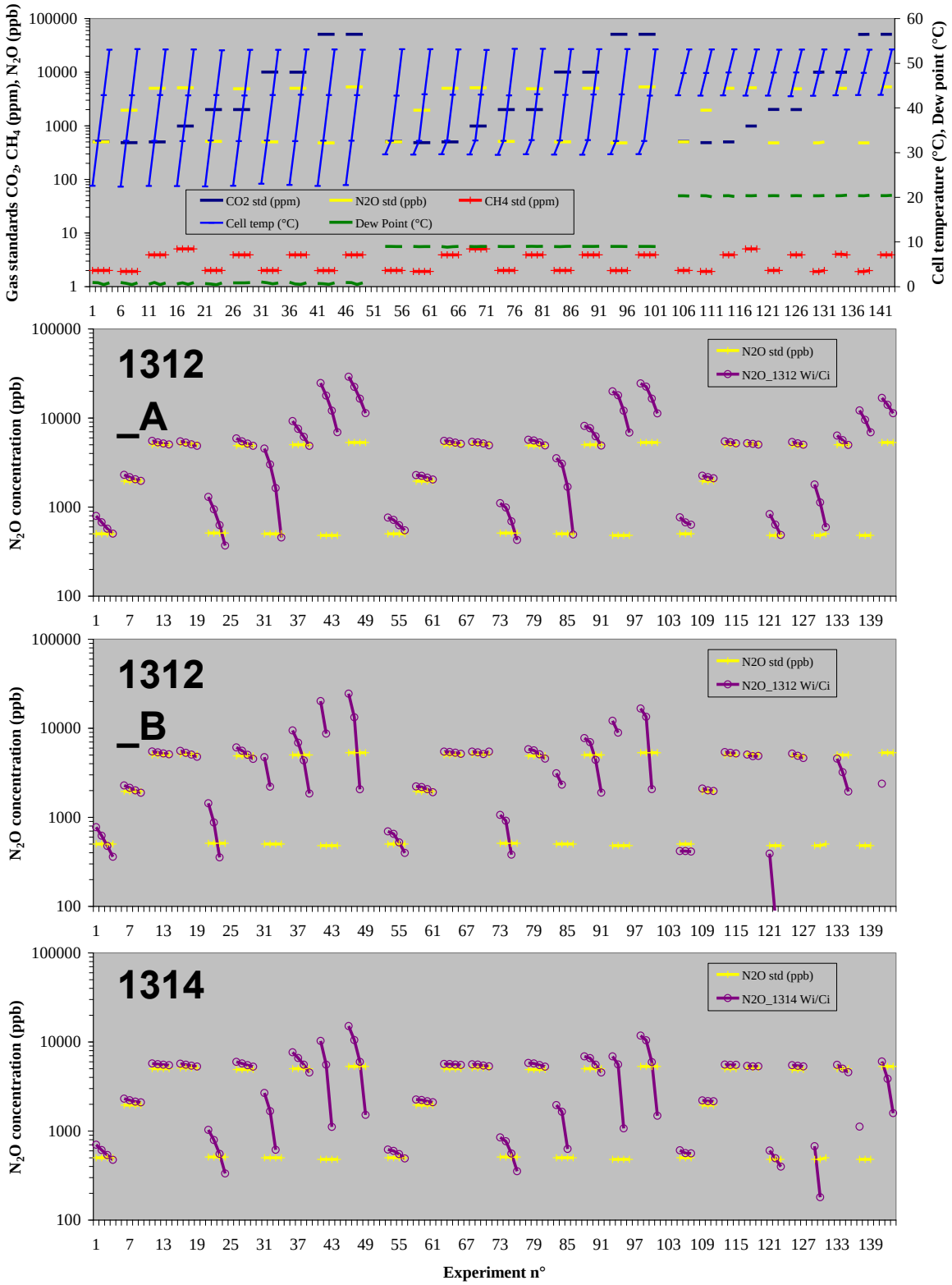

Figure 3b N2O concentration determined by the Innova's instruments. The number on the x-axis refers to trials with conditions as given in the first panel. The solid lines in the panels indicates the applied standard gas concentration for N2O

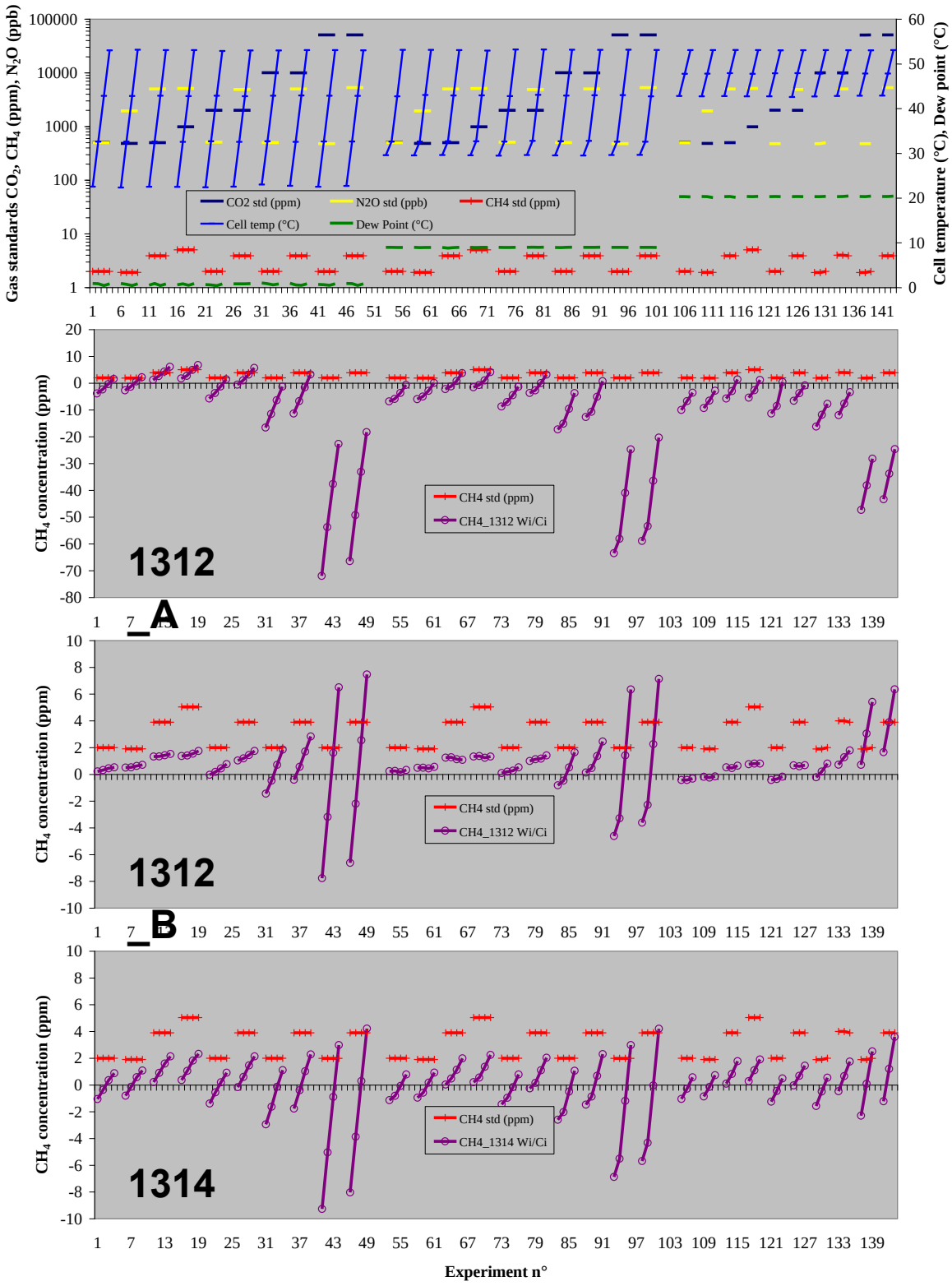

Figure 3c CH4 concentration determined by the Innova's instruments. The number on the x-axis refers to trials with conditions as given in the first panel. The solid lines in the panels indicates the applied standard gas concentration for CH4.