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# *MEASUREMENT OF HYDROGEN CONCENTRATION IN THE ATMOSPHERE - COMPARISON OF DIFFERENT DETECTION METHODS*

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Hydrogen is a minor atmospheric constituent. The globally averaged atmospheric mixing ratio of $H_2$ fluctuates at present around 500ppb. The sources and sinks of hydrogen are not well quantified. The transition to hydrogen economy will inevitably result in large disturbances of hydrogen budget, both on global and regional scales, with potentially serious consequences for oxidative capacity of the atmosphere. It is therefore necessary to monitor $H_2$ mixing ratios in present-day atmosphere with highest precision available. The EU 6th Framework Project EUROHYDROS is aimed at initialising European monitoring capability for atmospheric hydrogen, including the ability to derive isotope ratios and to use these observations, together with studies on sinks and sources of $H_2$ and modelling work, to improve the understanding of hydrogen budget.

Most measurements of atmospheric mixing ratios of hydrogen to date have been performed with the aid of gas chromatographic separation and detection using RGA detector. Another potential methods for detection and monitoring of atmospheric concentrations of $H_2$ include Electron Capture Detector (ECD) doped with nitrous oxide, as well as Pulse Discharge Helium Ionisation Detector (PDHID). A systematic

comparison of the three methods of $H_2$ detection mentioned above is presented. The following parameters were considered: (i) limit of detection, (ii) linearity of the detector, (iii) reproducibility of analyses for ambient range of hydrogen concentrations, (iv) suitability of the method for continuous monitoring, (v) investment and operational costs. The investigated detectors where checked for linearity of the $H_2$ signal in the range between 200 and 1000 ppb. In case of ECD, the flow rate of doping gas ($N_2O$) turned out to be crucial for achieving adequate reproducibility and linearity of the detector. The temperature of ECD and the flow rate of carrier gas are another important parameters in measurements of atmospheric $H_2$ mixing ratios using this detector. While gas chromatographs equipped with PDIHD and ECD detectors revealed good long-term stability with respect to monitoring of atmospheric hydrogen, the RGA detector turned out to be sensitive to changes of external conditions such as room temperature and ambient pressure variation. On the other hand, the RGA detector is insensitive to presence of moisture in the sample, while the air injected to gas chromatograph equipped with PDIHD detector has to be devoid of water. This requirement introduces additional complications of the analytical system. The ECD detector is sensitive for both $H_2O$ and $CO_2$ traces in the analysed air. The RGA detector revealed the lowest detection limit for hydrogen (less than 100ppt) among the studied detection systems. However, its linearity is rather poor, particularly for low $H_2$ mixing ratios. The two other detectors tested (ECD and PDIHD) exhibit excellent linearity for wide range of hydrogen concentrations.

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