Problems of Perfecting and Metrological Assurance of Laser Gas Analyzers

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In view of the need of ambient air quality control, occupational health control, authenticity of food and gases, and for medical purposes, laser gas analyzers must provide high accuracy of measurement. Development of metrological traceability of measurement for carbon monoxide, carbon dioxide, methane, formaldehyde, and carbon dioxide isotopes ratio laser gas analyzers is discussed in this presentation.

Laser gas analyzers provide detection of very small concentrations of target gases with high accuracy and small response time. Cavity Ring Dawn Spectroscopy (CRDS) method of attenuation of a laser beam in a cavity resonator is developing very fast. Recently a big number of papers were published in scientific journals. According to the online subscription-based scientific citation indexing service (Web of Science) about 1500 papers are already published on the subject, three fourth of which last ten years, and half of papers last five years. An interest to this method of measurement is growing.

Modern technology provides mirrors reflection coefficient in a resonator about 99.999%. Application of such mirrors ensures multiple reflection of laser beam inside of a resonator (about 100000 times) and as a result provides total optical path length about 20 km (for a length of an optical chamber 25 cm). Inserting target gas into this multi-path optical chamber (MPOC) decreases time of laser beam attenuation and accordingly decreases time of signal attenuation. Comparison of attenuation time without target gas and with target gas in MPOC gives an opportunity to measure the concentration of target gas.

CRDS gas analyzer has high precision of measurement, very lower detectable limit, and short response time. Precision of measurement of this type of gas analyzer depends on the precision of measurement of time of signal attenuation in a resonator which in turn depends on resonator dimensions, mirrors reflection coefficient, and electronics of gas analyzer.

Very big total optical path length provides an opportunity to measure small optical absorption and leads to high precision measurement e.g. of $^{13}$C/$^{12}$C isotopes ratio (standard deviation $\delta^{13}$C according to our investigation is about 0.3%). Because of the fact that $^{13}$O$_2$ molecule has different mass from $^{12}$O$_2$ molecule their absorption lines do not coincide in spectra. The ratio of these molecules in gas mixture can be found by measuring intensity ratio of absorption lines of these isotopes. The problem was to measure weak $^{13}$O$_2$ absorption line (concentration of $^{13}$O$_2$ in total CO$_2$ volume is about 1%) against closely situated spectra intensive $^{12}$O$_2$ absorption line. This problem is resolved by the CRDS method.

The analysis of matrix effect (matrix - gas which is contained in gas mixture with target gas, e.g. nitrogen, helium, air) on the measurement of target gas concentration is presented in this work. Time of signal attenuation at the same optical wave length is different for different matrixes in gas mixtures so giving not equal measured concentrations of target gas for different matrixes because different matrixes broaden absorption line of target gas in a different way and because the absorption line shape of target gas becomes deformed when using different matrixes in gas mixtures. A possible way to solve this problem is finding a scaling ratio for different matrixes.

In view of the need of ambient air quality control, occupational health control, authenticity of food and gases, and for medical purposes, laser gas analyzers must provide high accuracy of measurement. It should be mentioned that carbon dioxide isotopes ratio laser analyzer can reveal piracy products of juice, vine and the other alcoholic beverage as well as its source of origin. It can differentiate natural gas and bio-methane and it can detect Helicobacter pylori bacteria in human being. Analysis of patient’s expired air gives an opportunity to identify serious maladies in an initial stage.

Development of metrological traceability of measurement for carbon monoxide, carbon dioxide, methane, formaldehyde, and carbon dioxide isotopes ratio laser gas analyzers is also discussed in this presentation. The next measures are used to provide metrological traceability of measurement for just listed components:

1. Use of commercial gas mixtures of methane, carbon monoxide, carbon dioxide, and carbon dioxide containing specified $^{13}$O/$^{12}$O isotopes ratios.
2. Use of commercial permeation tubes with formaldehyde.
3. Chemical purity of these samples is assessed with known uncertainty by analysis of foreign components (impurities).
4. Gas mixtures with specified total concentrations of target gas and specified $^{13}$O/$^{12}$O isotopes ratios are prepared according to ISO 6142 and ISO 6143 standards using gravimetric method.