RAMAN SPECTROMETER FOR ANALYSIS OF GASEOUS MIXTURES

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A Raman spectrometer (RS) for analysis of gaseous samples has been developed. Test results are presented.

Feasibility of simultaneous analysis for a number of components contained in gaseous mixtures without sampling is a very serious argument in favor of the RS method despite small nonresonant Raman scattering cross sections and weak optical signals. The Raman method for analysis of gaseous molecular mixtures is being increasingly used with advances of development of electronic and optical elements in spectrometers. This method allows one to analyze not only gaseous mixtures. For example, a lidar[1] harnessing this method is capable of analyzing emissions from stacks of heat-and-power stations (HPSs) and other industrial objects at distances up to 1 km at night when meteorological situations are favorable. However, it is not always possible to use lidars due to their technical complexity and dependence of their operation upon the environmental conditions. Therefore, it is of interest to analyze samples of gaseous mixtures taken by special sondes placed, for example, inside stacks of industrial enterprises.

In the present paper, the model of a Raman spectrometer developed for analysis of samples of gaseous mixtures simulating smoke plumes from industrial enterprises has been considered. A solid-state pulsed laser and a TV photon counter (TPC) were taken as a basis of the spectrometer.

The block diagram of the Raman spectrometer is shown in Fig. 1. The laser radiation with the wavelength $\lambda = 0.53$ μm was directed into a cell filled with an examined gaseous mixture. Scattered radiation entered a polychromator through an objective lens, cutoff filter, and light guide and then entered a photocathode of a composite photodetector. Such a photodetector built around a supervidicon and a range-gated brightness amplifier is capable of recording single-electron events.[2] Television signals from photoelectron scintillations were selected and processed to determine the position of their center of gravity in the photocathode plane and then were recorded in multichannel memory. Synchronization of the spectrometer elements was performed by a timing generator.

Dispersion of the polychromator having a diffraction grating with 1200 lines/mm and the brightness amplifier photocathode 14 mm in diameter allows us to record simultaneously the spectrum range $\Delta\nu = 600$ cm^{-1} and consequently the complete Raman spectrum of gases at four fixed angles of the diffraction grating rotation. Therewith, signals could be calibrated against either oxygen ($\nu_R = 1556$ cm^{-1}) or nitrogen ($\nu_R = 23331$ cm^{-1}).

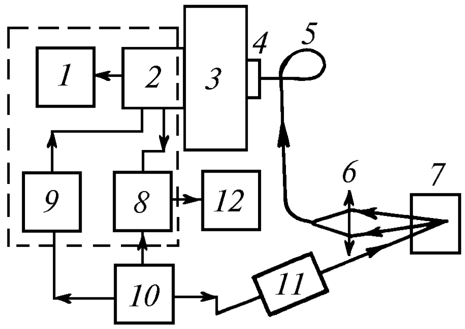

FIG. 1. Block diagram of the Raman spectrometer: video monitor 1, composite photodetector 2, monochromator 3, cutoff filter 4, light guide 5, receiving objective lens 6, cell with examined gaseous mixture 7, multichannel memory (AI-1024 pulse analyzer) 8, strobe-pulse generator 9, synchronizing block 10, ILTI-408 solid-state laser 11, and plotter 12.

The spectrometer was equipped with two cells whose designs are shown in Fig. 2. The additional window was used in the cell *A* to put the laser radiation in thus decreasing the fraction of radiation scattered at the laser wavelength by cell elements. The walls of the cell *B* were blackened and it had a light trap for the same purpose.

As a result of laboratory tests, the minimum detectable concentration of a number of gases being typical atmospheric pollutants should be determined. In particular, the following gases were chosen: hydrogen sulfide, nitrogen oxide, sulfur dioxide, and methane. Hydrogen sulfide and methane were purchased by us at industrial enterprises and special chemical reactors were made to obtain nitrogen oxide and sulfur dioxide. To prepare the working gaseous mixtures, we applied the following procedure: The above-indicated gases were reduced 100 times with technical-grade nitrogen in special tanks. Then required gaseous mixture was composed in the cell by taking manometer readings and the air was added to atmospheric pressure. The initial content of gases in the cell was determined by manometer readings and during the experiments it was monitored by signals recorded from N_2 and O_2 and from examined component. The test results of the RS with the cell *A* are tabulated in Table.I.

Results summarized in Table I were obtained at a laser pulse repetition frequency of 12.5 Hz with pulse energy of 5 mJ. Exposures indicated in Table I are optimal because their further increase did not improve the signal-to-noise ratio. The noise level was measured for the cell filled with technical-grade nitrogen. The minimum detectable gaseous concentration exceeds significantly its values expected from statistics of photoelectron counts. Both factors are indicative of occurrence of the correlated optical noise. We assume that it is due to the cell imperfection producing significant noise signal due to both laser radiation scattering and fluorescence of quartz walls. Results of analysis of model gaseous mixture in the cell *B* are given in Table II.

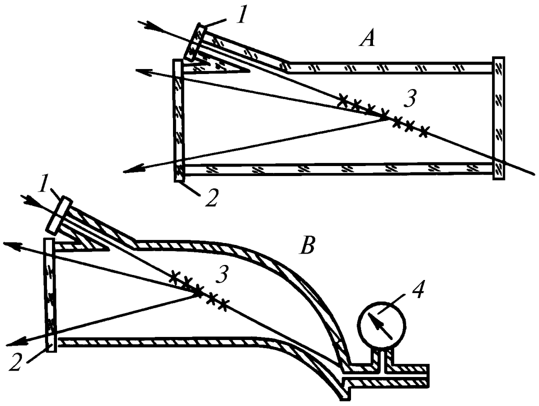

FIG. 2. Cells for gaseous mixture analysis: input window for laser radiation 1, exit window for scattered laser radiation 2, zone of gaseous mixture analysis 3, and manometer 4.

TABLE I.

Gaseous component	Minimum detectable concentration, %	Signal-to-noise ratio	Measurement time, min
SO_2	0.15	3	5
NO_2	0.10	3	2
CH_4	0.23	6	2
H_2S	0.18	3	5

TABLE II.

Gaseous component	Minimum detectable concentration., %		Signal-to-noise ratio	Measurement time, min
	Measured	Calculated		
N_2	57	–	5	0.5
H_2O	$31.0 \cdot 10^{-2}$	$30.0 \cdot 10^{-2}$	3	7
SO_2	$2.3 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	3	5
NO_2	$2.3 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$	3	2
CH_4	$4.6 \cdot 10^{-2}$	$5.0 \cdot 10^{-2}$	6	2
H_2S	$2.3 \cdot 10^{-2}$	$5.0 \cdot 10^{-2}$	3	5

Data about the Raman cross sections of some gases normalized to the N_2 cross section were used to determine the concentration. The spectral characteristics of the polychromator and the brightness amplifier photocathode were assumed linear in the given spectral range. As is seen from Table II, in this experiment the noise signal was about an order of magnitude lower than that in the experiment with the cell *A*.

In connection with the fact that signals from N_2 and pollutants were essentially different, we limited the exposure time by 14096 pulses. Taking into account spectral position of the Raman lines the SO_2 and H_2O signals were calibrated against O_2 and H_2S

and CH_4 signals were calibrated against N_2. Measurements of the H_2O density were carried out with the use of the coefficient of the calibration against the O_2 and N_2 signals.

In summary, it should be noted that a combination of modern solid-state lasers and multichannel photon counters built around microchannel brightness amplifiers and CCDs (charge coupled devices) makes possible Raman spectrometers whose specifications are much better than known ones.[3] In particular, it is possible to develop portable Raman spectrometers.

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