Raman gas analyzer applicability to monitoring of gaseous air pollution

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ABSTRACT

It is shown that the main problem, arising when designing a stationary Raman gas analyzer intended to monitor gaseous air pollutions, is to get SRS signals of sufficient intensity. The engineering solutions are presented that provide the required sensitivity (~ 50–100 ppb). It is achieved by compressing a gas medium under analysis and gaining intensity of the exciting laser radiation.

Raman spectroscopy, gas analysis.

1. INTRODUCTION

Diagnostics of the composition of gaseous media at a new technical level are greatly needed in today's society. Environmental protection agencies and agencies of the Ministry for Civil Defense, Emergencies, and Disaster Response especially need high-sensitivity monitoring instruments solving problems for both environmental monitoring of atmospheric pollution and identifying emergency situations associated with emission of toxic gases into the atmosphere. In connection with development of the corresponding instrumentation, refining analysis methods, and improving metrological characteristics of gas analyzers, the list of their fields of application is steadily expanding.

Despite the broad range of physical principles for monitoring gaseous media and instruments based on them, optical diagnostics methods are especially important. This is because of their high sensitivity, selectivity, and speed at which results are obtained. The most attractive optical diagnostics method is spontaneous Raman scattering (SRS) spectroscopy. The SRS method for gas analysis makes it possible to simultaneously record any molecular components of the gaseous medium using a single laser with fixed wavelength, where the SRS signal for each gaseous component is strictly individual, proportional to its concentration, practically instantaneous, and does not depend on the composition of the gaseous medium. Owing to such a unique set of properties, the SRS method is a general-purpose optical method for analysis of multicomponent molecular gaseous media, including media whose composition is not known ahead of time. The major disadvantage of this method is the low intensity of the SRS signals in a gaseous medium, due to the low density of molecules and the small light scattering cross section ($\sim 10^{-30}$ cm^2/sr). However, when using high-sensitivity multichannel photodetectors, and also with improved efficiency of detection of the SRS signals, the possibility arose to design a high-sensitivity SRS spectrometer and an SRS gas analyzer.

2. RAMAN GAS SPECTROMETER SRS-02

At the laboratory of Ecological Instrumentation of IMCES SB RAS in recent decade a prototype has been developed of a stationary gas analyzer operating on SRS. Such a gas analyzer has a number of advantages over the existing analogs. First, using one fixed-wavelength laser, we can simultaneously monitor all molecuar components exceeding a detector' sensitivity thershold and investigate gas media with unknown composition, second, it does not need consumables and, third, it has quite high operational efficiency. Note, that despite known difficulties due to weak SRS signals, we achieved some promising results when we have developed SRS-02 SRS gas analyzer for natural gas analysis. This gas analyzer in continuous operation allows determining all molecular components, which content exceeds 50-100 ppm[1, 2].

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Fig. 1. Raman gas analyzer SRS-02.

3. NEW MODIFICATION RAMAN GAS ANALYZER SRS-03

Besides, our team have developed and tested on the atmopsheric and expired air the SKR-03 model that has a sensitivity of less than 1 ppm for methane[3]. This is a record experimentally-proved sensitivity value for sich gas analyzers. This device consists of the small-size DPSS laser (1 W, 532 nm), the high pressure gas cell (40 bar), specialized spectral device, CCD matrix and manual pneumatic pump[4].

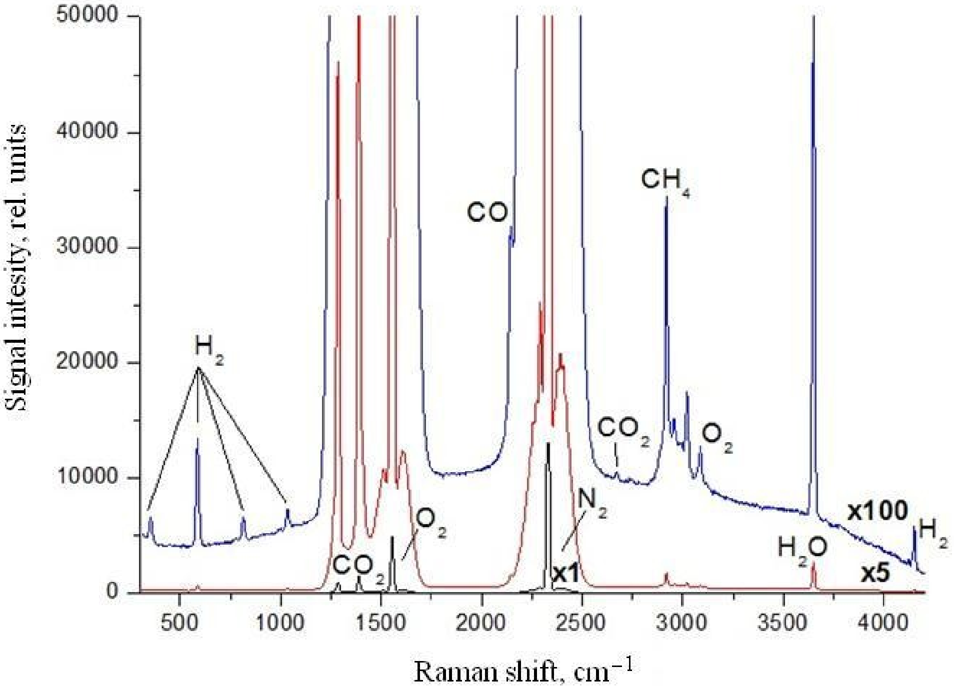

Fig. 2. Raman spectrum of the air that was breathed out by smoking man

Figure 2 snows the recorded Raman spectrum of the air that was breathed out by a smoking man on 1:1, 1:5, and 1:100 scales. This spectrum was obtained using Raman gas analyzer SRS-03. In addition to components of atmospheric air (nitrogen, oxygen, carbon dioxide, water vapor, and methane), the breathed out air consists of the *S*-branches of the rotational spectrum (354, 587, 814 and 1033 cm^{-1}) and *Q*-branch of vibrational-rotational spectrum (4156 cm^{-1}) for H_2, increased concentrations for CH_4 (2917 cm^{-1}) and CO_2 (1285 and 1385 cm^{-1}), the *Q*-branch of the vibrational band (2143 cm^{-1}) for CO, the *Q*-branch of vibrational band (2671 cm^{-1}) for overtone CO_2 and others. Furthermore, in the spectrum there are characteristic bands for the gaseous components at frequencies 2740, 2955, 2990, and 3020 cm^{-1} that need more detailed identification.

4. PATHS OF INCREASING SENSITIVITY

For ecological monitoring of gas atmospheric pollution the SRS analyzer sensitivity should be no less than instantaneous maximum permissible concentrations (MPCs), that is 1-2 orders of magnitude higher which was obtained for gas analyzer SRS-03. In this paper we estimate feasibility of such a SRS gas analyzer. Table 1 lists the most abundant atmospheric air components and gas pollution to be monitored.

Table 1. Raman frequencies (ν) and relative normalized differential cross-sections (σ) of the main atmospheric components [5]

Component	**ν (cm^{-1})**	**σ**
Nitrogen, N_2	2331	1
Oxigen, O_2	1555	1
Hydrogen, H_2	4156	3.9
Carbon oxide, CO	2143	0.9
Water vapor, H_2O	3652	3
Carbon dioxide, CO_2	1388 1285	1.1 0.8
Methane, CH_4	2917 1535	8 0.1
Nitrogen oxide, NO	1877	0.4
Nitrogen dioxed, NO_2	1320	13
Methanol, CH_3OH	2846	5
Sulfur dioxed, SO_2	1151	4
Ammonia, NH_3	3334	6.1
Formaldehyde, CH_2O	3121	>1
Hydrogen sulfide, H_2S	2611	6.8
Benzene, C_6H_6	3070	14
Toluene, $C_6H_5CH_3$	1003	>1

According to MPCs indicated in the Table 1, required gas analyzer's sensitivity should be of ~50–100 ppb.

Analysis of Table 1 shows that all components listed are of molecular architecture and in the frequency shifts of 0–4200 cm^{-1} they have characteristic rotational-vibrational SRS bands, therefore they can be detected. Thus, the main problem in SRS gas analyzers' development is to obtain sufficient SRS signal intensity. However, according to SRS line intensity ratio [5], it can be improved due to the following :

1) exciting (laser) beam power multiplication;

2) increasing of scattering particles' concentration in the scattering volume.

Sensitivity increase may be achieved by both using a higher energy laser and appliance of a specially designed multipass small-size cell [6], as well as by compressing of a gas media to be analyzed.

Experience in SKR-03 operation implies that, all other things being equal, at laser power of 1 W, analyzed mixture pressure of 40 bar and one-pass cell, a realized sensitivity on methane was 1 ppm (differential cross-section σ~8). Now, in the system under development, we suppose to use a 10 W-laser, a multipass (20 passes) cell, as well as to compress analyzed gas medium up to 100 bar.

Table 2. Specifications of SKR-03 and SKR-04* prototypes

Characteristic	**SKR-03 [3]**	**Gas analyzer under development (SRS-04*)**
Laser power (I)	1 W	10 W
Pass number (n)	1	20
Pressure (P)	40 bar	100 bar
Solid angle (Ω)	Not changed	Not changed
Scattering cross section (σ) component for sensitivity assessment	8 (CH_4)	0.4 (NO)
Sensitivity realized (*U*)	1 ppm	–

Let us estimate a possibility to attain sensitivity of ~50÷100 ppb on the required gas components. Since threshold sensitivity (*U*) is proportional to reciprocal signal-to-noise value (*S*/*N*), then

$$U'/U \sim \frac{S/N}{S'/N'}, \tag{1}$$

where asterisks mark values for the system to be assessed, while values without asterisks are experimentally-confirmed. At a first approximation, noises in this formula are determined by a receiver’s noise, so we can consider them equal because in a gas analyzer under development we will use the similar photodetector. Keeping this in mind and substituting signal value equal to SRS line intensities in Formula (1), we obtain:

$$\frac{U'}{U} \sim \frac{S}{S'} = \frac{In\sigma P\Omega}{I'n'\sigma' P'\Omega'}, \tag{2}$$

where *I* is exciting radiation power, *n* is number of laser radiation passes inside a cell, σ is differential scattering cross-section, *P* is gas pressure in a cell, Ω is solid angle in which scattering radiation is collected. Given that angle Ω is fixed, let us substitute in Formula (2) the values listed in Table 2. Note, that this estimation should be done for the component having minimum differential cross-section (~0.4 for nitrogen oxide). Finally, we obtain

$$U' \approx U\frac{In\sigma P\Omega}{I'n'\sigma' P'\Omega'} \approx 1ppm \cdot \frac{1W \cdot 1 \cdot 8 \cdot 40bar}{10W \cdot 20 \cdot 0.4 \cdot 100bar} \approx 40ppb\,. \tag{3}$$

Judging from Formula (3), we can expect that, since gas components listed in Table 1 have higher scattering cross-sections, minimum detectable concentrations for them would be lesser, thus, their excess over MPC would be detected.

CONCLUSION

Assessments show that multicomponent stationary SRS gas analyzer intended for air pollution monitoring can be created and implemented.

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