Photoionization microplasma sensor

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Abstract. New developments in the physics of plasma are presented, specifically, research of completely new method of atoms' and molecules' detection in gaseous phase – collisional electron spectroscopy. As a result, the microplasma sensor for quality and quantity analysis of the gaseous mixture was created. It works in the discharge afterglow mode using He as a buffer gas. In addition, the modification of the sensor using resonance photon photoionization was developed. This consideration gives the opportunity for wide practical appliance as an individual gas analyzer for industrial and medical purposes.

1. Research method and its actuality
Method CES (collisional electron spectroscopy) is patented in Russia 2217739; the USA 7,309,992; Japan 4408810; China ZL200380106502.2; Germany 503 14 126.7; France EP1557667 and Great Britain EP1557667. This method allows to analyze gas mixtures at a high pressure up to atmospheric one without vacuum, using electron spectroscopy [1]. It is based on the fact, that only the value of characteristic electrons' energy needs to be measured, not the momentum vector value [2].

1.1. Review of traditional spectroscopy methods
Well known that to identify atoms and molecules in electron spectroscopy measurement of electrons energy released during ionization of atomic or molecular impurities A by particles B* with definite energy $E_p$ (photons, quick electrons, excited atoms, etc.) are taken.

$$A + B^* \rightarrow A^+ + B + e$$  \hspace{1cm} (1)

After the collision the kinetic moment of appeared characteristic electrons is determined using various energy analyzers. Based on these results the energy value is calculated ($m$-particles' mass, $v$-particles' speed, $p$-particles kinetic moment).

$$E = \frac{m v^2}{2} = \frac{p^2}{2m}$$  \hspace{1cm} (2)

Ionization potential $E_i$ of atoms or molecules A is found by measured energy $E_e$ (electrons' specter) and definite energy $E_p$ of particles $B^*$ and then these atoms or molecules are identified.

$$E_i = E_p - E_e$$  \hspace{1cm} (3)

Consequently, to determine electron energy in the traditional spectroscopy methods it is necessary to use high vacuum and bulky energy analyzers to disperse electrons in 'kinetic moment - coordinate' space, for example, cylindrical or sphere mirror, electrostatic or magnetic lenses, time-of-flight tube and etc. Here, electron is flying out from the starting point with the definite momentum vector, then diverges to the analyzer field, and gets to the calculated according to the motion equations detector's
point. In reality, mentioned energy analyzers determine kinetic moment of the electron, based on which the starting kinetic energy is calculated.

Any collision of the identifying charged particle with atoms or molecules of residual gas leads to particle scattering and, so, to 'leaving the game' or wrong detection in unpredictable receiver point with the loss of resolution capability.

Additional technical and methodical problem is the sample's (which is under atmospheric pressure) atoms or molecules insertion into analyzer's space, where high vacuum is required.

This leads to the increase in mass, size, energy consumption and technical complexity of the traditional ways of gaseous mixtures' composition determination, which doesn't provide the solution for various important analytical challenges that modern science is facing.

1.2. Collisional electron spectroscopy

The basis for the proposed detection method is the fact that during one elastic collision of the electron with gas particles, it loses only small part of its initial kinetic energy. That's why, if during the movement toward the detector, electron goes under 100 elastic collisions, it completely 'loses' initial trajectory of its kinetic moment (like during Brownian movement), but at the same time its energy distortion will make relatively small part <1%.

This peculiarity of detection method allows to refuse from using electron energy analyzers with high vacuum and bulky construction for space electron dispersion, depending on its kinetic moment, and replace it with two plane parallel electrodes with pulse-actuated plasma between them. It significantly decreases the size and mass of the sensor, and as a consequence, its cost. Because of this, the size of the sensor CES is about 10*10*1 mm.

Determination of electron's energy in method CES is done by registration of the second derivative of electrons' current on the analyzing electrode, depending on counter potential. Characteristic energy $E_e$ of the electrons, which are formed during the ionization of the additives, according to (3) can lie in the range from 0 up to the energy of actuating particle, depending on the ionization potential of the additive. It is possible to assume that the highest limit for applicable energies of actuating particles should be equal to the ionization energy of buffer gas atom, because in case of use of actuating particles with higher energy, ionization of the main gas will start, which will cause troubles in determination of the additives. Therefore, measuring current-voltage characteristics in the range of applied voltage from 0 to the ionization potential of the main gas atom, it is possible to find the electron distribution speed function $F(v)$ (and also relative electron energy distribution $f(E_e)$) and the number of the electrons, which occur because of the particular additive ionization, using Druyvestein’s formula for plane probe.

$$ F\left(\frac{2eU}{m}\right) = \frac{4m}{e^2 \cdot S \cdot N_e} \cdot U \cdot \frac{d^2 I_e}{dU^2} $$

Here $e$ – electron charge; $U$ – voltage, applied to the electrodes; $S$ – electrode area; $I_e$ – electron current on plane cathode; $N_e$ – electron concentration

Therefore, the second derivative of current-voltage measurement gives a curve, which contains peaks, each of which corresponds to the group of characteristic electrons produced by ionization of a particular additive. Energy of these electrons $E_e$ and score of relative peaks in the range of applied voltage are determined by formula (3). Mentioned two-phased derivation can be done using different methods, including straight numerical derivation of the current-voltage measurement, using, if necessary, various ways of data smoothing. Different electronic circuits can be applied, which use modulation of applied voltage $U$ with small $\Delta U$ with frequency $\omega$ and current registration on frequency $\omega$ for 1st derivative and $2\omega$ for the 2nd.
2. Microplasma sensor CES

Microplasma sensor is developed based on this method. It operates in the discharge afterglow mode. Electron energy spectrums of He as a buffer gas under different pressures and with various electrodes' distances are gotten [4].

Equipotentiality of the ionization camera's space, where ionization collisions occur, is provided by creation of afterglow plasma in the ionization camera between two plane parallel electrodes with the help of impulse source of energy (figure 1). During the afterglow of impulse discharge, after cooling of charged particles and when electro-neutral conditions are attained by plasma, almost equipotential space is leveling off in the camera between anode and cathode. At the same time, energy of the electrons, which occur as a result of additives' ionization, doesn't depend on coordinates of the point, where they occur.

The relation between concentrations of main gas and analyzing additives should be so, that major part of occurring metastable atoms is composed of buffer inert gas atoms. At the end of the discharge, quick 'decay lag' of all excited atoms will take place, and the afterglow plasma will mostly consist of metastable atoms of buffer gas with definite energy $E_p$. Helium atoms' energies are 19.8 and 20.6 eV, which is enough to ionize almost all known atoms and molecules.

To measure the spectrum of characteristic electrons probing pulse is applied on anode with dwell time after charge impulse. The voltage of probing pulse gradually changes with each charge impulse. The current on the cathode during probing pulse is measured, and as a result current-voltage characteristic is plotted in the range from 0 V to ionization limit of the main gas. Then the second derivative of $I-U$ characteristic is taken and the spectrum of characteristic electrons, which occur in discharge afterglow as a result of analyzing atoms collision with metastable He atoms, is calculated. Ionization potentials of analyzing atoms is determined by electron energy spectrum and definite energy of ionization metastable atoms. Analyzing atoms are identified based on their ionization potential.
3. Photoionization microplasma sensor

Absolutely new construction of the VUV-photoionization CES detector was developed to use it as a portative gas analyzer for continuous personal biomedical diagnostics [5]. This way energy spectrum of electrons, occurred in the ionization with resonance photons, which wavelength is situated in the vacuum ultraviolet (VUV), is measured. Nowadays, micro plasma source of such photons on resonant line of Kr with energy of 10.6 eV is developed.

Electrons’ energies analyzing is done in simple gas-filled block with additional grid between anode and cathode, where additives ionization is happening with a use of outside VUV-emission. In this case, full energy of the electrons, occurred in different parts of the grid, is determined by its characteristic kinetic energy. Gradually changing negative voltage is applied to the cathode, electron current is measured and \( I-U \) characteristic is plotted.

VUV-photoionization detectors CES have a big advantage in comparison with to all other detectors, where electron impact ionization is used. The reason for this is the fact, that only analyzing additives are ionized and detected using VUV-emission, main air components (oxygen, nitrogen) remain neutral, because their ionization potential is higher than VUV-photons' energy. This helps to decrease background signal, increase sensitivity and resolution capability.

Sensitivity limit of CES detectors is assessed by photoionization cross-section for detecting additives and VUV-photons' flow. According to the estimation, during the emission flow in order of \( 10^{14} \) photons/sec through photoionization zone and with sensitivity of recording equipment of current on the level of \( 10^{-12} \) A, the detection limit for molecules, which have a cross-section on resonant line of Kr or Ar is few digits in order of \( 10^{-19} \) cm\(^2\), is about 0.1 ppm [6]. Work to further increase the sensitivity of the CES detectors by higher-aperture detector's construction and increased sensitivity of electrometer amplifiers, is in progress. The watt consumption may comprise less than 1W.

Numerical tests were done to assess the accuracy of the detection method [7].

The experimental model of photoionization sensor CES was developed and constructed (figure 2) [8].

![Figure 2](image)

**Figure 2.** The experimental model of photoionization sensor CES

Supposed photoionization sensor CES characteristics are shown in the Table 1.
Table 1. Supposed photoionization sensor CES characteristics

| Characteristics                          | Value   | UM  |
|-----------------------------------------|---------|-----|
| Limit of the small additives detection | 1,00    | ppm |
| VUV-quantum energy                      | 10,6    | eV  |
| Sensitivity of photocurrent, no less than | 1,00    | pA  |
| Resolution on photoelectrons' energy    | 0,10    | eV  |
| Overall volume                          | 100,00  | cm³ |
| Watt consumption, no more than          | 1,00    | Watt|
| Maximum working temperature             | 50,00   | °C  |
| Minimum working temperature             | -30,00  | °C  |

Sensors, based on CES method, will be widely popular in industrial field, transportation, safety and ecological control systems, because of its small size and low cost. Nevertheless, it is possible to develop portative device for continuous personal biomedical diagnostics, because of its wide range of detectable molecules and high accuracy. Such sensor can become the base of the future preventive medicine [9].

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