Prospecting of the collision electron spectroscopy method and its integration into personal microplasma photoionization sensor CES

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Abstract. The method of Collision Electron Spectroscopy (CES), which allowed the plasma research group of St. Petersburg Mining University to develop an innovative photoionization sensor, has several applied advantages over existing analog molecular detection methods currently used at enterprises. Though, the rate of global consumption of products manufactured at enterprises increases, which has a high risk of threat to human life and health, most developers are not able to meet the increased level of international quality standards for measuring instruments. The CES method not only makes it possible to increase the accuracy of modern measuring equipment at times, but makes the gas analyzer device portable, increases autonomy, and also significantly reduces the device’s dimensions, which, as a result, allows the device to be used as an individual portable sensor and used for diagnostics health conditions at home.

1. Introduction
The 21st century is the time of a large number of diverse methods of gas analyzing. However, the new time requires completely new highprecision approaches in the detection of molecules. A new approach that changes the concept of molecules detecting is the Collision Electron Spectroscopy (CES) method; the operation principle of the CES microplasma photoionization sensor is based on it. The proposed detector has several advantages, including small dimensions, reasonable price (in comparison with similar market segments), high sensitivity and a wide range of detectable molecules. In addition to a significant number of advantages of the CES sensor, the functional multitasking of the device should be noted. This device has an application in the healthcare sector as a personal analyzer and as a tool for monitoring human health, in the manufacturing sector as a tool of monitoring the health status of staff, in the mining industry, as a devise for established control of drilling-and-blasting operations. In addition, the CES microplasma photoionization sensor has a domestic application, it can be used as a tool for gas leaks detecting. Thus, the CES detector is a unique tool that has found application in many areas of human life. So it is able to save human’s life.

The sensor is very cross functional thanks to the Collision Electron Spectroscopy method.

2. Collision Electron Spectroscopy method
The Collision Electron Spectroscopy (CES) method is based on the process of registration of characteristic electrons’ energy, which is formed as a result of ionization of the analyzed gas. The CES
method allows abandoning the measurement of the particle momentum vector, which, due to the uselessness of installing less accurate vacuum equipment, significantly reduces the mass and dimensions of the device [1].

Thus, when atoms and molecules collide with photons that have an energy of 10.4-11.5 eV, the length of which is located in the vacuum ultraviolet region the analyzed gas is ionized, which leads to the creation of free characteristic electrons. Gas discharge sources with a MgF for generating krypton resonance radiation on atomic lines of 116.48 nm (10.64 eV) and 123.58 nm (10.03 eV), inside which a cylindrical cathode and anode (Figure 1) are filled with buffer gas and accepted as photon initiators. A sample of such a gas is the Kr-He mixture.

![Figure 1. Discharge lamp and electrodes](image)

Besides, it should be noted that the control of the device is fully coordinated by the programmed microprocessor circuit (Figure 2), the modes of which were determined in the laboratory. The startup voltage on a krypton gas discharge tube is 500 V, a constant-burning mode is 250 V. Currently, the sensor recognizes about a hundred different molecules, which confirms its high competitiveness.

![Figure 2. Photoionization sensor CES with microcontroller ADuC-841](image)

To maintain the high-quality characteristics of the device, a unique constructive layout of the
internal sensor elements was developed. (Figure 3). The variable geometry of the CES ionization chamber was formed by two cylindrical electrodes 5, 6 made of steel, which were mounted in a cell 8 made of molybdenum glass with a diameter of 30 mm and a length of 200 mm, mounted horizontally. The outside diameter of the cylindrical electrodes is equal to the inner diameter of the cuvette, one of the electrodes 1 is fixed in the cuvette, and the second electrode 2 can freely slide on slight friction along the cuvette so that the required distance between the electrodes can be set using an external magnet. The ends of the cylindrical electrodes facing each other had a flat shape and were perpendicular to the axis of the electrodes, thus forming a planar configuration of the CES microplasma detector. The cylindrical electrodes were connected to electrical inputs 9,10 of molybdenum wire and soldered to the ends of the cell, moreover, the electrode 6 was connected to the input 9 through a flexible nickel tape 11 folded in accordion, which allowed the electrode to move freely along the cell.

![Figure 3. The CES detector ionization chamber diagram](image)

The cuvette is filled with spectrally pure helium, which is additionally purified by passing through a cryogenic trap. The system provides the possibility of the discharge tube working both in the flow mode (pumping speed v ~ 1-10 m/s), which makes it possible to remove from the discharge zone the products of dissociation of molecules and in the mode without gas flowing through the discharge pipe.

In order to provide the mode of formation of the electron energy distribution function, with the help of an external magnet, the distance between the ends of the cylindrical electrodes was established based on the calculation of the “controlled death” mode of characteristic electrons on the electrodes or walls of the ionization chamber of the CES detector, until these electrons lose a noticeable part of their initial kinetic energy.

The advantage of this gas analyzer is its wide range of applications. In response to the software developed on the base of the ADuC-841 microcontroller in Assembler, the operator can adjust the basic parameters of the device, calibration of the sensor is performed once, it allows one to analyze multicomponent mixtures. However, during detecting an air mixture for exceeding the maximum permissible concentrations of molecules of a known harmful gas, the operator can adjust the main parameters: set the scanning step, scanning limits of the cathode voltage, scanning step, duration of the photocurrent measurement interval and the number of repetitions of the photocurrent measurement.

In order to obtain the energy spectrum of electrons from the current-voltage dependences measured by the CES detector, it is necessary to find the second derivative of this dependence. Among the various possible approaches, we chose the option of prepartitioning the measured curve into intervals, smoothing the data within each interval with conditions for maintaining of certain smoothness at the ends of the intervals and then differentiating the smooth curve, where the influence of finite-difference instabilities is much less pronounced [2].

For the numerical approximation of the experimental data, the programs from the ALGLIB package were used to construct a regression spline in the form of a piecewise-defined third-degree polynomial, with the two neighboring polynomials on the boundary stitched so that the resulting function is continuous and has a continuous first derivative.

To select the regularization parameter, it is also possible to apply an algorithm using the Fisher criterion, where the number of statistically distinguishable linear parameters was determined from the change in the residual sum of squares deviations of the model curve from experimental data.

When the process of scanning is completed, the received data is transmitted via RS-232 to the
computer, where, the second derivative of the current-voltage curves and the energy spectrum of the characteristic electrons are obtained. Processing of the results is summarized on the basis of the software developed under Windows OS. Among a number of well-known algorithms for numerical differentiation, a spline approximation was chosen with minimization of the squares’ sum of the spline deviations from the original curve and the subsequent differentiation of the smooth curve already found.

The ADC provides digitalization of the photocurrent with a frequency of up to 300 kHz over a given period of time, averaging of obtained results and increasing in the signal-to-noise ratio. The length of the photocurrent integration time was controlled by a timer, which is built into the ADuC-841 and issuing an interruption after the accumulation interval closing to set the following value on the cathode and transition to a new point of the current-voltage curve.

![Figure 4. Current-voltage curve, first and second derivatives, atmospheric air sample](image)

Furthermore, the data smoothing mode and display of the 1st and 2nd derivatives of the smoothed curves are being set using the additional differentiation menu. By pressing the mouse button, the left and right borders of the “current-voltage” curve are set. This site is been exposed to smoothing and subsequent differentiation. The abscissa axis of the graphic window shows the scanned voltage at the detectors’ anode. The voltage corresponds to the energy of the characteristic electrons. The source data of the measured current-voltage characteristic, the smoothing approximation spline, the 1st derivative inverted relative to the x-axis, and the 2nd derivative of the smoothing curve, which corresponds to the desired spectrum of the characteristic electrons, are simultaneously displayed in different colors on graphic (Figure 4).

3. Discussion
Modern devices which are used in the oil and gas industry are not able to provide the necessary level of accuracy in determining the molecular concentration of harmful substances hazardous to the health of employees. However, the principle of operation of the CES microplasma photoionization sensor, based on the Collision Electron Spectroscopy method, reduces energy output and increases particle recognition accuracy. The latter aspect is a mandatory requirement for a modern high-tech device as a portable gas analyzer. The result was achieved due to the rejection of a top-heavy structure of vacuum equipment, which allows achieving the maximum effect in oil and gas processing conditions when the device is used for continuous monitoring of maximum permissible concentrations of noxious...
substances, environmental spikes, oxygen in the fluids of kilns, flare gas and combination strings. The main difference between the microplasma sensor CES and the previous generations of gas analyzers is the registration principle. The sensor measures only the energy of the characteristic electrons, but not the magnitude of their momentum vector.

Besides, the use of a plane-parallel two-electrode configuration of the CES microplasma detector provides the maximum limitation of the ionization zone metal surfaces that provide an irrevocable exit of the electron from the game when it hits them, which is necessary to create conditions for the nonlocal regime of the afterglow plasma in the detector ("controlled diffusion"). Also, the detector configuration provides the maximum possible current of characteristic electrons to the analyzing electrode - up to half of all characteristic electrons can reach on the analyzing electrode if the transverse dimensions of the electrodes are much larger than the distance between them. This allows one to get the maximum sensitivity and the best possible signal-to-noise ratio for the gas analysis method.

In the laboratory experiment, the electrodes gap was used in the range from 2 to 20 mm, and, accordingly, the helium pressure in the cell was from 5 to 40 Torr. The selected geometry of the CES microplasma detector made it possible already at this stage to increase the operating pressure when measuring in comparison with the traditional versions of the Langmuir probe method, which operates at a pressure of the main gas of no higher than 3-5 Torr. This circumstance is since in the traditional probe scheme it is impossible to effectively limit the diffusion range of characteristic electrons until they hit the probe, which leads to an increase in the contribution to the probe current of those electrons that were born far from the probe, and to the moment of contact with the probe their kinetic energy was strongly “degraded” in collisions and significantly distorted compared to the initial one.

When an electron collides with gas particles on the way to the anode, it completely loses the original direction of the pulse, while the kinetic energy changes by a relatively small amount <1%. Thus, the registration of the kinetic energy of free electrons does not significantly affect the sensitivity of the device. Lack of necessity to maintain a high vacuum allows this approach to reduce the size of the sensor, maintaining high accuracy and sensitivity, which makes this device non-replaceable as a portable gas analyzer that provides a high level of safety in oil and gas and mining industries.

4. Application

Many people face a large number of different diseases daily. The situation is complicated by the fact that more than 30 percent of people do not seek medical help in a timely manner. And at the time of treatment complications are found that require serious medical intervention. Timely diagnosis of the disease is the basis of easy recovery. The proposed photoionization sensor CES is capable to analyse human’s health due to a wide range of detectable molecules. So, the fingerprint of diabetes is the appearance of acetone taste in the mouth, the CES sensor indicates an increase of the concentration of its molecules in the human body. The sensor recognizes acetone molecules from the total number of detected molecules and signals about increasing of acetone concentration, then the user can promptly seek medical help.

This personal analyzer has been widely applied in other areas. An application of the CES microplasma photoionization sensor in the production of gas and oil companies, with allowance for a wide range of advantages over the models used: the small size of the device, a wide range of detectable molecules, flexibility of configuration, low expected cost of up to 800 $, high sensitivity (1 ppm and better). This device is able to displace traditional gas analyzers, that are based on obsolete technologies because of its multipurposeness. The dimensions of the CES gas analyzer are comparable to the dimensions of pen, it make possible to talk about its use as an individual device (built into a silicone bracelet) for detecting and preventing dangerous concentrations of various harmful gases in the atmosphere situated near a face of oil or gas wells or at other technological sites in the oil and gas sector.

CES detector is promising in the mining industry. It can replace the expensive and low-performance equipment used for making aerological mine maps. The device also perfectly suits the
role of an individual sensor of environmental air quality, which is especially relevant for employees of mining enterprises working near the mine face. The developed CES analyzer detects the presence and quantity of gas molecules in the air, compares admissible values and signals about critical values that allows one to start the gas clearing in time.

It is also possible to use the microplasma gas analyzer CES at customs control points for noncontact monitoring, its high sensitivity makes it possible to detect vapors of various substances including their minimum concentrations in the air.

5. Results

By now, the following results were achieved in the framework of scientific research:

- a schematic diagram of the VUV photoionization detector has been developed with a source of ultraviolet photons as a miniature gas discharge tube. This tube has been made with MgF2 end window and has been filled with Kr-He mixture to generate the resonance radiation of krypton on the 116.48 nm atomic lines (10.64 eV) and 123.58 nm (10.03 eV). A cylindrical cathode and an anode have been mounted inside a 16 mm glass bottle, the radiation has been discharged through the end of the anode; discharge voltage has been 450 V, burner voltage has been 220 V, discharge current has been 3 mA, consumed power has been less than 1 W;
- operating modes have been selected, namely in the gas discharge chamber there has been an inert gas under pressure from 102 Pa to atmospheric one. The discharge voltage has been 300-500 V, the current has been about 10 mA;
- based on the microcontroller ADuC 841 a model of a microprocessor system has been manufactured and assembled. It has controlled the power system for the discharge ignition in a constant mode on a high-voltage DC-DC converter (adjustable output up to 500 V), block of step-by-step digital scanning of the delayed voltage in the range 0-5 V with a scanning step of 0.01 V, an ADC that provided digitization of the photocurrent with a frequency of up to 300 kHz and averaging the samples obtained;
- the software for the ADuC-841 microcontroller (embedded software) has been developed in the Assembler language that provided an opportunity for the operator to determine the scan limits of the cathode voltage, the scanning step, the duration of the photocurrent measurement interval at each scan step and the number of repetitions of the photocurrent;
- based on the previously created software package for processing spectral data, a prototype software for processing the "current-voltage" curves has been developed for Windows OS;
- the grafen coating of the electrodes have become an innovation, that made it possible to reduce the work function of electrons to 1 eV, it has been described in more detail in the article [3];
- sensitivity of the CES VUV photoionization detector was increased by reducing the background signal;
- the energy distribution function of electrons was analyzed in the VUV photoionization variant of the CES detector. The energy of VUV photons is 10.5-11.5 eV, sufficient for ionization of a wide range of organic molecules. It allows one to approach the GC MS method in terms of informativity but exclude expensive highvacuum equipment [4];
- based on the results of computer simulation of helium plasma in the CES detector, the distributions of the concentration of electrons, atomic and molecular ions, metastable and lower excited states of the main gas, and also the electric field both in the active phase of the discharge and in the afterglow with time resolution are obtained. It is shown that the calculated plasma concentration profiles and electric fields correspond to the proposed theoretical principles of operation of the microplasma detector;
- the CES method was used to measure the energy spectra of characteristic electrons generated in a pulsed discharge at a gas pressure of 5-40 Torr in collisions of metastable helium atoms with each other and upon collisions of the second kind with electrons, as well as xenon spectra in helium;
- a small admixture of M was added to the buffer helium. Next, a full-scale simulation of the discharge parameters was carried out, results made it possible to determine the value of the useful
signal and evaluate the analytical capabilities of the studied analysis method (Figure 5).

**Figure 5.** The current-voltage characteristic of the detector, its first derivative, and the electron energy spectrum (pressure He – 5 Torr, the distance between the detector electrodes – 10 mm)

The presentation based on the materials of this research was made and presented at the international conference "59th Annual Meeting of the APS Division of Plasma Physics", Milwaukee, Wisconsin in October 2017.

6. Conclusion
Collision Electron Spectroscopy method is a method of the future that does not require expensive equipment for its implementation in contradistinction to modern methods of studying the properties of materials in the field of materials science, energetics and ecology [5]. The study of the basic physical aspects of this technology made it possible to obtain a similarity rule as a dependence between the concentration of the test gas, the length of the interelectrode gap and the level of distortion of the electron energy spectrum. The equipment based on this method has minimal dimensions, high sensitivity (1ppm) and low power consumption. It makes the microplasma sensor unique and competitive in the gas analyzer segment of market.

The results of computer simulation of helium plasma in the detector made it possible to construct the distribution spectra of characteristic electrons, atomic and molecular ions, and lower excited and metastable states of the main gas [6-9]. During the research works, it was found, that the calculated profiles of plasma concentration and electric fields correspond to the principles of operation of the photoionization detector CES.

The uniqueness of the microplasma sensor CES consist of a significant number of advantages that are very important for the production processes, as a means of ensuring the safety of stuff in industrial facilities. The future lies with technologies that protect the interests of people, protecting their health, therefore microplasma photoionization sensor CES is the technology of the future, which will become a personal tool for monitoring the health status of each person.

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