# Development of the plasma electron spectroscopy method for the detection of complex chemical compounds

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The expansion of the capabilities of the plasma electron spectroscopy method for the analysis of complex chemical compounds and their fragments has been demonstrated. Since the energies of the detected Penning electrons are different for different chemical compounds, an important advantage of the method used is the possibility of simultaneous (in one measurement) registration of various impurities. The developed microplasma detector can serve as a prototype of a gas analyzer based on non-local negative-glow plasma of a short glow discharge in helium.

**Keywords:** plasma electron spectroscopy method, electron energy distribution function, gas analysis, plasma diagnostics.

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The application of plasma electron spectroscopy (PLES) for the detection of impurities in buffered helium is one possible solution to the problem of developing miniaturised and technically simple gas analyzers (see, for example, the paper [1] and references therein).

The PLES method is based on the registration of selective groups of fast electrons $e_f$ formed in the Penning ionization reactions of impurities $A$ by metastable helium atoms (or molecules) He*:

$$\mathrm{He}^* + A \rightarrow \mathrm{He} + A^+ + e_f(E_p). \qquad (1)$$

The energy spectra of electrons born in reactions (1) are narrow peaks near the energy of their occurrence $E_p = E^* - E_i$ on the electron energy distribution function (EEDF) [2].

Since the $E_i$ ionization potentials of any atom or molecule are well known and vary between substances, by measuring the $E_p$ Penning electron energies and using the known $E^*$ excitation potential of triplet (19. 82 eV) and singlet (20.6 eV) metastable helium atoms, it is possible to identify the atom or molecule $A$ of unknown impurities by their ionization potential $E_i = E^* - E_p$ [eV] (qualitative analysis). From absolute measurements and/or calibration of the signals from these peaks, $A$ impurity densities can be found (quantitative analysis).

The concentration of metastable helium atoms can be determined from the corresponding peaks from the Penning ionization reaction between two metastable helium atoms $\mathrm{He}(2^3S_1)$ and from the superelastic collisions of metastable $\mathrm{He}(2^3S_1)$ atoms with slow electrons.

By now, the feasibility of impurity detection by PLES has been demonstrated for impurities of various atoms and molecules, including noble gases (Ar, Kr, Xe), metals (Pt), molecules $N_2$, $O_2$, CO, $CO_2$, $CH_4$, $C_2H_4$ and $NH_3$.

In the present work further possibilities of using the method of plasma electron spectroscopy for the detection and identification of complex chemical compounds and their components are demonstrated.

The experiments were carried out in miniature discharge tubes with tungsten electrodes of radius 1.5 mm. An additional electrode (wall probe) made of molybdenum wire with a diameter of 0.3 mm in the form of a ring with a radius of 1.5 mm, which was placed in the middle between the electrodes, was used for measurements. The interelectrode gap $L$ varied from 1 to 4 mm depending on the gas pressure. During the experiment, weak pumping was performed by continuously pumping and inflating gas from the cylinder through a needle inflator. As before in [1], measurements were carried out in a short (no positive column) glow discharge. A regulated DC source (0−1500 V), was used to ignite it, and a variable ballast resistor $10^3-10^5\ \Omega$ was used to protect the circuit and control the change in discharge current.

The Langmuir probe method of the second derivative of the current on the $V$ probe potential (see, e.g., [3]) was used to measure the EEDF and Penning electron spectra. As in [1], a commercial probe system from „Impedance“ [4] with the ability to automatically clean the probe surface with ionic current was used in the present work to measure the EEDF. The frequency control range of the generated signal could be varied from 1 to 100 Hz, and the duration control range of the generated signal was 1−8 ms. The signal was accumulated, and then the average value of the probe volt-ampere characteristic during $\sim 2-5$ s was already output. The amplitude„saw“ of the applied probe displacement was $\pm 30$ V.

Typical results of measurements of the second derivative of the probe potential in helium with small impurities of complex chemical compounds are presented in the figures. On the EEDF, maxima appear at characteristic energies corresponding to the Penning ionization (1) of atomic and molecular impurities by metastable helium atoms.

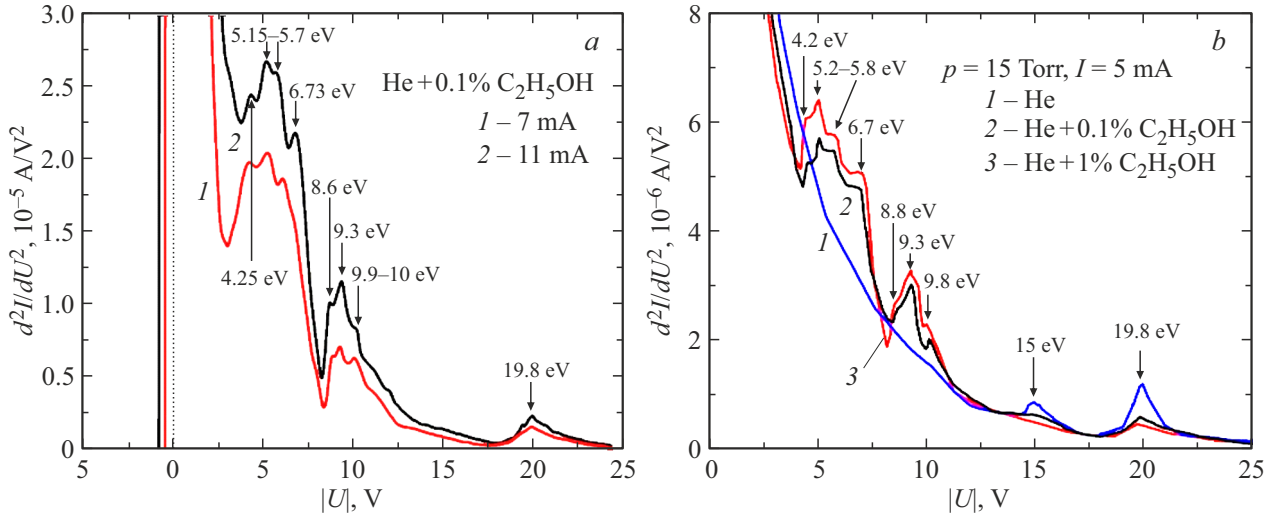


**Figure 1.** Measurement results for He + 0.1% $C_2H_5OH$ mixture at $p = 4$ Torr pressure and various discharge currents (*a*), as well as for pure He (*1*) and He + 0.1% $C_2H_5OH$ (*2*) and He + 1% $C_2H_5OH$ (*3*) pressure of$p = 15$ Torr and a discharge current of 5 mA (*b*).

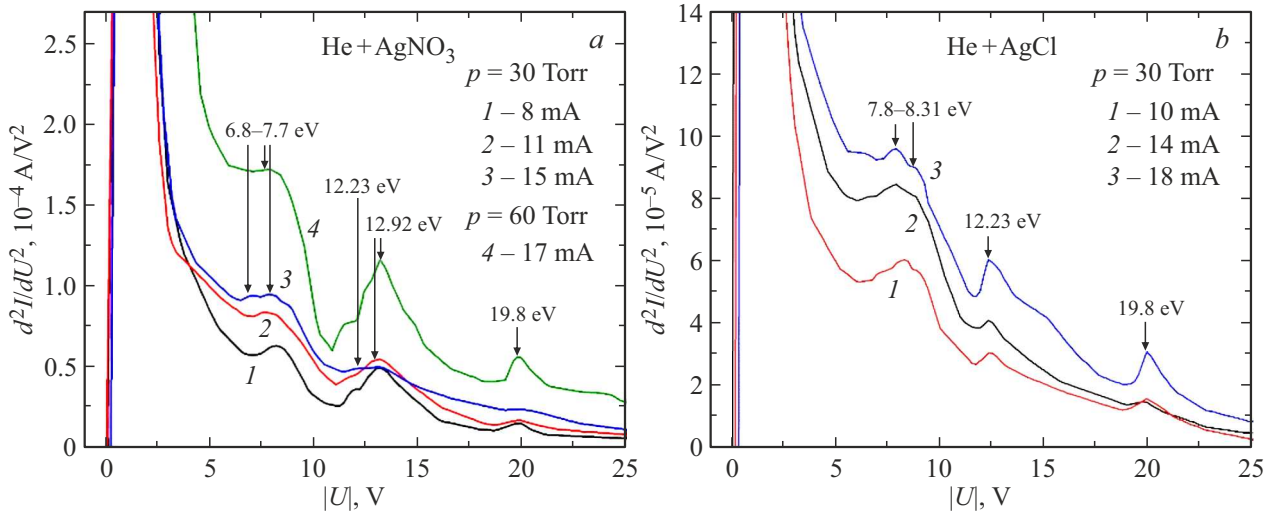


**Figure 2.** Measurement results for a mixture of helium with silver nitrate micropowder ($AgNO_3$) at $p = 30$ Torr (interelectrode gap $L = 3$ mm), $p = 60$ Torr ($L = 2$ mm) and different discharge currents (*a*) and for a helium/silver chloride micropowder mixture at $p = 30$ Torr ($L = 3$ mm) and different discharge currents (*b*).

Fig. 1 shows the results of measurements in the discharge plasma of a gas mixture of helium with a small admixture of alcohol (He + 0.1% $C_2H_5OH$ and He + 1% $C_2H_5OH$) at different pressures and discharge currents.

At first glance, only peaks from Penning ionisation reactions between two metastable helium atoms at energy 14.5 eV and from superelastic collisions of slow electrons with metastable helium atoms at energy 19.8 eV, as well as from Penning ionisation (1) of alcohol molecules by metastable helium atoms, are to be expected

$$\mathrm{He}(2^3S_1) + \mathrm{C_2H_5OH} \rightarrow \mathrm{He} + \mathrm{C_2H_5OH^+} + e\{9.3\,\mathrm{eV}\} \quad (2)$$

with a peak at 9.3 eV. However, as a result of plasma chemical reactions in the discharge, multi-atomic molecules with large molecular masses can form various secondary products. In result various peaks of characteristic electrons are observed, obtained by the collision of the excited helium atom with various radicals — products of alcohol cleavage:

$$\mathrm{He}(2^3S_1) + \mathrm{CH_3} \rightarrow \mathrm{He} + \mathrm{CH_3^+} + e\{9.8\,\mathrm{eV}\}, \quad (3)$$

$$\mathrm{He}(2^3S_1) + \mathrm{CH_2} \rightarrow \mathrm{He} + \mathrm{CH_2^+} + e\{8.8\,\mathrm{eV}\}, \quad (4)$$

$$\mathrm{He}(2^3S_1) + \mathrm{CO_2} \rightarrow \mathrm{He} + \mathrm{CO_2^+} + e\{6.7\mathrm{eV}\}, \quad (5)$$

$$\mathrm{He}(2^3S_1) + \mathrm{CO} \rightarrow \mathrm{He} + \mathrm{CO^+} + e\{5.8\,\mathrm{eV}\}, \quad (6)$$

$$\mathrm{He}(^3S_1) + \mathrm{H_2} \rightarrow \mathrm{He} + \mathrm{H_2^+} + e\{5.2\,\mathrm{eV}\}, \quad (7)$$

$$\mathrm{He}(^1S_0) + \mathrm{H_2} \rightarrow \mathrm{He} + \mathrm{H_2^+}(vibrate) + e\{4.2{-}4.25\,\mathrm{eV}\}. \quad (8)$$

In the next step, studies for silver nitrate crystals ($AgNO_3$) were carried out in a similar manner (Fig. 2, *a*). Peaks in the region 19.8–20.6 eV from collisions of metastable helium atoms with slow electrons are observed. In addition, peaks are observed at 6.8–7.7 and 12.23–12.92 eV. They are caused by the decomposition of silver nitrate

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2 \quad (9)$$

and subsequent Penning ionization of volatile vapors of silver nitrate decomposition products in buffered helium

$$He(2^3S_1) + NO_2 \rightarrow He + NO_2^+ + e\{12.92\,eV\}, \quad (10)$$

$$He(2^3S_1) + O_2 \rightarrow He + O_2^+ + e\{7.7\,eV\}, \quad (11)$$

$$He(2^3S_1) + Ag \rightarrow He + Ag^+ + e\{12.23\,eV\}. \quad (12)$$

It should be noted that the peak at 12.23 eV really corresponds to the ionisation of silver atoms. This is also confirmed by the following experiment with silver chloride (AgCl) crystal micropowder. Thus, Fig. 2, *b* shows the results of measurements in negative luminescence plasma in helium with AgCl crystals. In addition to peaks at 19.8–20.6 eV, peaks at 12.23 eV and at 7.8–8.31 eV are observed. These peaks are due to the decomposition of silver chloride

$$2AgCl \rightarrow 2Ag + Cl_2, \quad (13)$$

$$He(2^3S_1) + Cl_2(vibrate) \rightarrow He + Cl_2^+ + e\{7.8\text{–}8.31\,eV\} \quad (14)$$

and subsequent Penning ionisation of silver and chlorine impurities in buffer helium. Thus, the work demonstrates the extension of the capabilities of the PLES method for the determination of small impurities of complex chemical compounds on the example of alcohol, as well as silver nitrate and chloride.

The presented results extend the nomenclature of the determined substances and allow to register both gases and volatile vapors of salt crystals in the nonlocal plasma of a short glow discharge as a result of their cathodic atomisation and decomposition into components.

Since the ionisation potentials of different impurities are different from each other, the PLES method can simultaneously detect multiple impurities in a single measurement.

A distinctive feature of the technique is the use of a rather simple scheme for recording the electric current from an auxiliary additional probe electrode while scanning the delayed electric potential. Therefore, this method will be very useful in building small-sized gas analyzers with a simple vacuum pumping system based on a miniature vacuum pump.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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