

Highfrequency discharge with a liquid electrode for spectral analysis of solutions

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A portable high-frequency pulse generator with a high-voltage output and ability to adjust the pulse output parameters over a wide range was manufactured. This generator was used to ignite an atmospheric high-frequency liquid-electrode discharge (RF-APLD), which burned stably for minutes between a metal rod and surface of an aqueous electrolyte solution. The RF-APLD spectrum was recorded. It was shown that, when an organic additive (polyethylene glycol) was added to the aqueous solution, lines from metals whose salts were present in the liquid appeared in the spectrum.

Keywords: high-frequency generator, atmospheric high-frequency discharge with a liquid electrode (RF-APLD), atomic emission spectroscopy (AES), electrolyte spraying, solution analysis, polyethylene glycol.

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Due to its high sensitivity and selectivity, optical emission spectroscopy is widely used in many fields, including environmental protection, forensics, and analyzing geological objects, food products, biological fluids and a great variety of technical materials [1]. Conventional optical emission spectroscopy relies on sophisticated instruments that are highly energy-consuming, difficult to operate, and cannot be used under field conditions [2,3]. In recent years, a new trend in spectral analysis of solutions is being intensely developed, which consists in using discharges on the surface of liquid to be analyzed. This approach allows for a significant simplification of the instrument, except for such a complex component of conventional spectrometers as the spray chamber. Jointly with miniature matrix spectrometers which have recently become widespread, such an instrument offers hope for creating a compact portable setup for spectral analysis of solutions. The crucial component of such an analyzer is a compact atomization/excitation source characterized by low energy consumption and needing no gas communications. The literature widely considers direct-current discharges, mainly the electrolyte-cathode glow discharge (ELCAD) [4–8]. This paper proposes a new source based on an atmospheric high-frequency liquid-electrode discharge (RF-APLD).

As a high voltage source, we have constructed a portable high-frequency pulse generator whose circuit diagram is given in Fig. 1.

The generator is created based on a half-bridge inverter circuit with two high-voltage *N*-channel silicon transistors TMOS Power FETs IRF840 (International Rectifier) connected in opposite directions. The switches have on-state resistance of $0.85\ \Omega$ and are capable of switching currents of up to 8 A at the potential difference of up to 500 V. The control element of the half-bridge inverter is a half-

bridge driver microcircuit with built-in oscillator IR2153D (International Rectifier).

The 220 V (50 Hz) AC mains voltage is rectified by a high-voltage diode bridge and charges the working capacitor to the constant voltage of 323 V. Once the working capacitor is charged, the driver's internal oscillator controlling the transistor gates is activated. The switches begin to alternately close the working capacitor to the load that is the primary winding of the step-up transformer; the secondary winding of the latter is the instrument output. The output signal is sinusoidal with the amplitude of 15 kV. The output signal frequency may vary from 1 to 500 kHz; measurements in this study were performed at the frequency of 100 kHz. The instrument has an additional input for controlling synchronization of the internal generator Sinc; using this input, it is possible to vary the output pulse parameters.

Fig. 2, *a* presents a schematic diagram of the experimental setup. 30 ml of electrolyte solution 9 consisting of distilled water with addition of 240 mM of HCl and 10 mM of KCl were put into plastic cylinder 10. Upper electrode 5 was made as a tungsten rod 2 mm in diameter enclosed in ceramic insulating sleeve 4, while the surface of liquid electrolyte 9 was used as the lower electrode supplied with current by immersing a stainless-steel wire 1 mm thick into cylinder 10. In the cylinder side wall, in parallel to the electrolyte surface, there was secured fiber optic input 7 of the Maya 2000 Pro spectrometer (8 in Fig. 2, *a*) used to record spectra in the range of 200–1100 nm. The spectrometer's instrument function width was 0.5 nm, the spectral sensitivity was adjusted at the manufacturer's and integrated into the instrument software.

After turning-on the power, diffuse torch 3 visually similar to the ELCAD torch arose between the metal electrode and liquid surface. Discharge region 2 with maximum

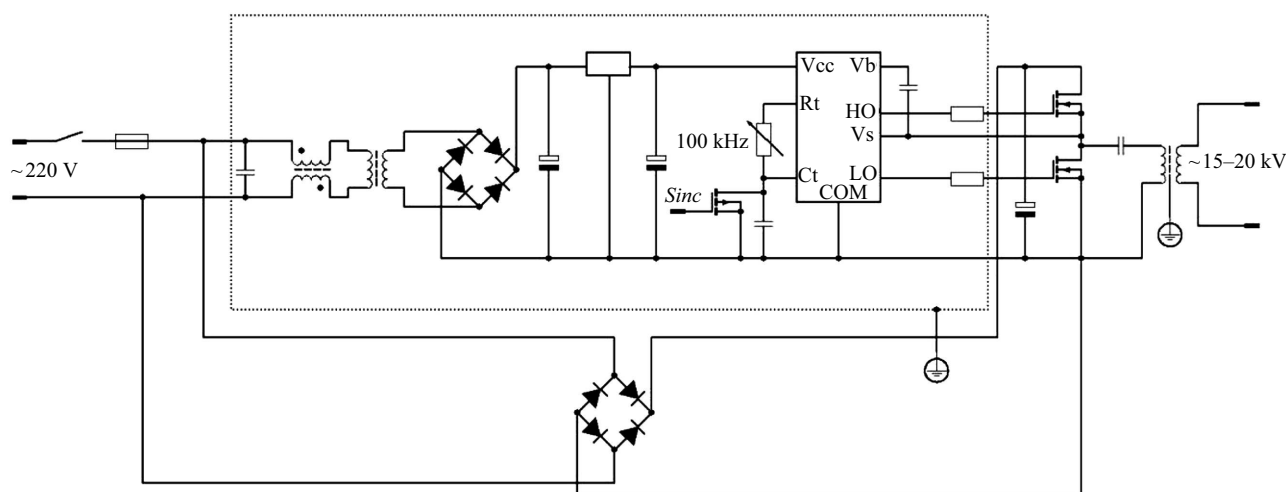


Figure 1. Circuit diagram of the high-frequency generator.

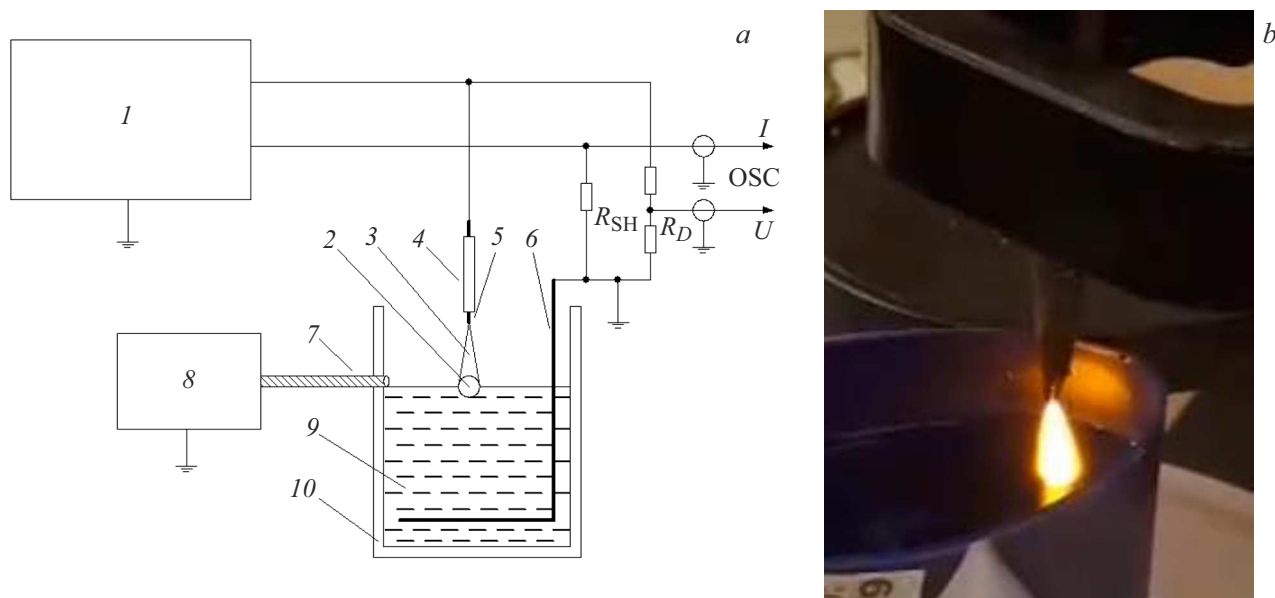


Figure 2. *a* — schematic diagram of the experimental setup: 1 — high-frequency generator, 2 — near-surface discharge region, 3 — atmospheric discharge region, 4 — ceramic insulator, 5 — tungsten electrode, 6 — lead wire, 7 — fiber optic input, 8 — spectrometer, 9 — electrolyte, 10 — plastic cylinder, R_{SH} — current shunt, R_D — voltage divider, OSC — detection system. *b* — a photo of the discharge on the electrolyte surface in the normal combustion stage.

luminosity was formed near the electrolyte surface. The gap between the electrode and solution was about 7 mm. Fig. 2, *b* presents a photo of the discharge on the electrolyte surface.

The setup electrical circuit is provided with voltage divider R_D and current shunt R_{SH} having coaxial outputs for connecting to detection system OSC consisting of the Tektronix TDS-220 digital storage oscilloscope with the bandwidth of 100 MHz and sampling rate of 1 GS/s per channel. The voltage and current oscillograms were obtained for the discharge burning above the supporting electrolyte surface; the oscillograms show that, in the gen-

erator's continuous operation mode, the discharge voltage magnitude was approximately 15 kV, while the current strength was slightly more than 3 mA. Thus, the RF-APLD electrical power did not exceed 45 W.

Fig. 3 presents the background emission spectra for the drop-spark discharge (DSD) and RF-APLD. DSD is a post-breakdown DC discharge between mutually approaching oppositely charged drops at the 2–3 kV voltage. The DSD duration is about 0.1 s; DSD differs from ELCAD (operating voltage of ~ 1 kV) in that the metal anode is replaced by an aqueous solution drop; however, this does not strongly affect the emission spectrum [9,10]. In both

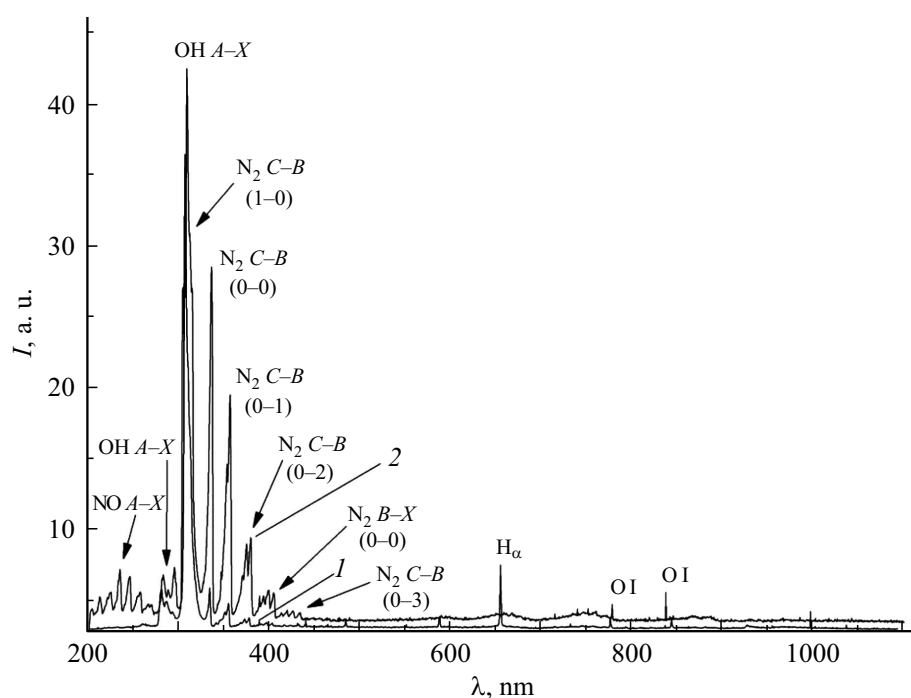


Figure 3. Emission spectra of discharges above the supporting electrolyte surface. 1 — drop-spark discharge, 2 — RF-APLD.

cases, a solution containing 120 mM of hydrochloric acid was used as the supporting electrolyte. The brightest spectrum component of both discharges is the hydroxyl OH ($A^2\Sigma^+ - X^2\Pi_{3/2}$) band belonging to the range of 306–320 nm. Fig. 3 shows that the spectra also contain the bands of nitrogen molecule N_2 ($C^3\Pi_u - B^3\Pi_g$) with the maxima at 337, 357 and 399.5 nm; their intensities are highest in the case of RF-APLD. Similarly to the ELCAD spectrum, spectrum of RF-APLD also exhibits the bands of nitrogen molecule NO γ ($A^2\Sigma^+ - X^2\Pi_r$), which are not observed in the DSD spectrum. On the other hand, the DSD spectrum contains clearly distinguishable Balmer-series hydrogen lines, whereas in the RF-APLD spectrum even the H_α band (656 nm) is almost invisible. Thus, the RF-APLD spectrum better represents the bands and lines of atmospheric components than those of water decomposition products, except for hydroxyl molecules. Apparently, the RF-APLD torch interacts with the liquid surface less strongly than the DSD torch.

It was shown that the DSD spectrum metal lines are enhanced many times by introducing into the electrolyte polyethylene-glycol-based surfactants [11]. Probably, the organic additive may enhance the metal salts transfer across the liquid–plasma interface because of intensification of the liquid thermal spraying [10].

Fig. 4 presents emission spectra of the discharge above the surface of electrolytes with different contents of polyethylene glycol (PEG-4000) that is an organic additive enhancing the intensity of the emission spectra of the elements under study. Fig. 4, *a* shows that, in the case of electrolyte free of PEG-4000, the RF-APLD spectrum does not contain

metal lines. The doublet of potassium lines K I 766.5 nm and K I 769.9 nm appears if 0.6 % of organic additive is added (Fig. 4, *b*). Figs. 4, *c* and *d* demonstrate further enhancement of these lines; evidently, in the presence of 4 % of PEG-4000 the potassium doublet is many times more intense than all the background components (the spectrum shown in Fig. 4, *d* also begins exhibiting the *D*-line of sodium existing as an impurity). This is caused not only by the enhancement of metal lines, but also by suppression of the hydroxyl and molecular nitrogen bands. Quenching of the background bands occurs due to introducing the organic matter and alkali metal into the RF-APLD torch, which reduces the plasma electron temperature. Thus, introduction of several percent of PEG-4000 for RF-APLD induces a qualitatively similar effect of metal lines enhancement that was observed for DSD after introducing a PEG-based surfactant [10]. The effect is probably connected with the organic additive influence on the aerosol spraying of the electrolyte cathode [11]; however, this issue needs further studies with various-nature discharges.

Tentative experiments with more concentrated inorganic and aqueous-organic solutions have shown that the RF-APLD plasma exhibits a higher resistance to variations in the liquid composition. A large voltage reserve and, probably, the AC mode prevent plasma breakdown typical of DC discharges in working with concentrated electrolytes and mixed solvents [11]. This makes RF-APLD a promising atomization/excitation source for the cost-effective portable optical emission spectrometer.

Thus, this study has shown a fundamental possibility of using RF-APLD as a source of atomization/excitation to be

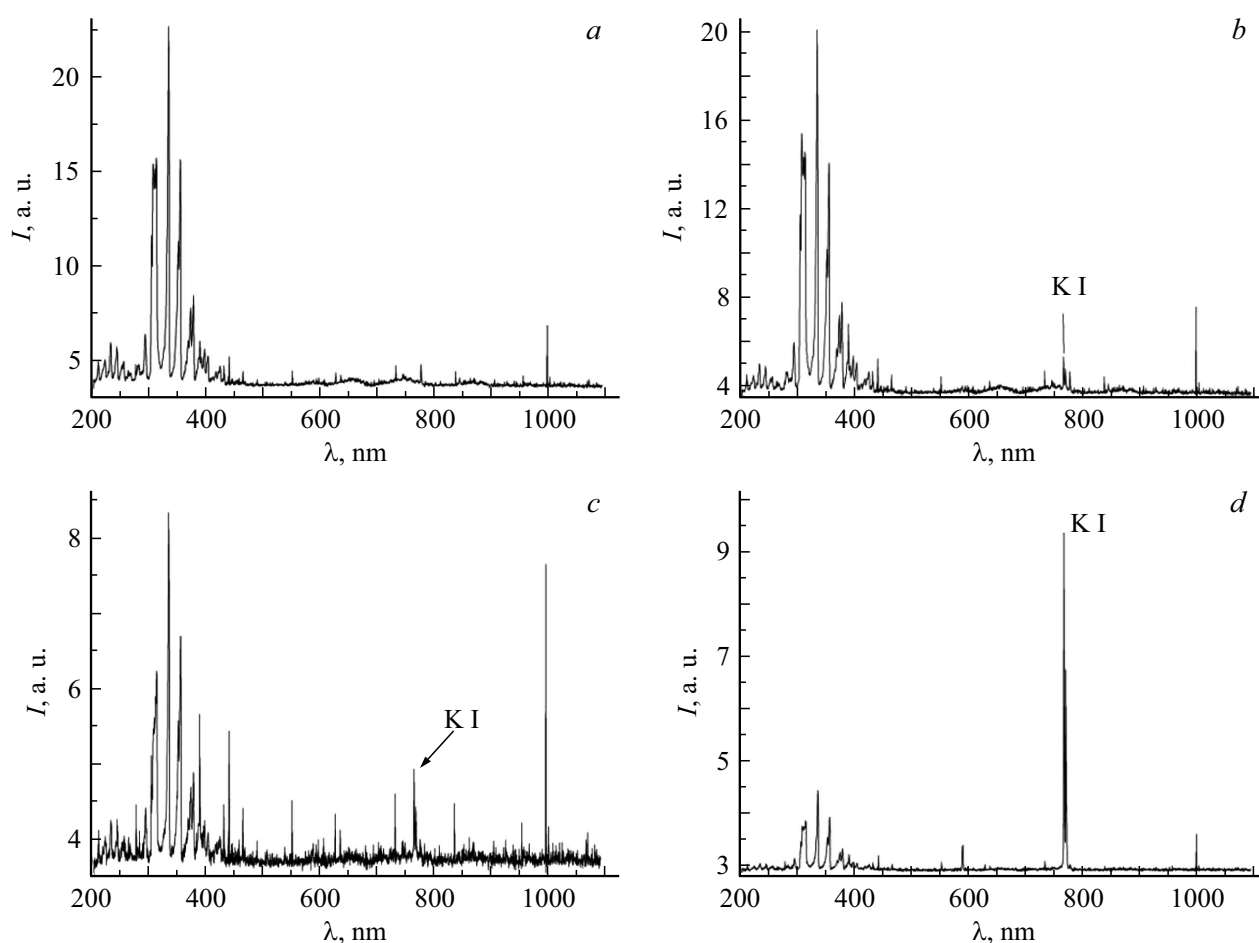


Figure 4. Emission spectrum of the discharge above the surface of electrolyte containing 240 mM of HCl and 10 mM of KCl. *a* — without additives, *b* — with addition of 0.6 % of PEG-4000, *c* — with addition of 1.6 % of PEG-4000, *d* — with addition of 4 % of PEG-4000.

utilized in atomic emission analysis of solutions. For this purpose, a portable high-frequency pulse generator with a high-voltage output was constructed. The influence of the PEG-4000 additive on the RF-APLD emission spectrum was studied, and the threshold nature of the PEG-4000 additive effect on enhancement of the potassium spectral lines and attenuation of the nitrogen and hydroxyl molecular bands was demonstrated.

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Conflict of interests

The authors declare that they have no conflict of interests.

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