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Application of a liquid electrode for collecting products of chemical reactions carried out in charged microdroplets of an electro spray torch

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Abstract. The experimental device for carrying out chemical reactions in charged microdroplets with the accumulation of reaction products and reactants in a liquid electrode was developed. The fundamental possibility of electro spraying a liquid onto the surface of a polar liquid (using acetonitrile as an example) in the modes of both positively and negatively charged microdroplets generation has been shown. In the mode of positively charged microdroplets generation, acidified acetonitrile was used as a sprayed solution; in the mode of negatively charged microdroplets generation, pure acetonitrile was used. In both cases, a stable electro spray mode was obtained over a wide range of the spraying voltage U (from 2.2 kV to 5 kV), the distance from the spraying capillary to the surface of the liquid electrode L (from 3 mm to 23 mm) and the sprayed solution feed rate Q (from 25 $\mu\text{l}/\text{min}$ to 200 $\mu\text{l}/\text{min}$). It was shown on the example of the reaction of phenylhydrazine with anisic aldehyde that the products of reactions occurring in charged microdroplets, as well as the reactants, accumulate in the volume of the liquid electrode.

Keywords: charged microdroplets, electro spray, condensation reactions, liquid electrode, mass spectrometry, high-performance liquid chromatography

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Материалы конференции

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Применение жидкого электрода для сбора продуктов химических реакций, проводимых в заряженных микрокаплях факела электроспрея

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Аннотация. Разработано экспериментальное устройство для проведения химических реакций в заряженных микрокаплях с возможностью накопления продуктов реакции и реагирующих веществ в жидком электроде. Показана принципиальная возможность электрораспыления жидкости на поверхность полярной жидкости (на примере ацетонитрила) в режимах генерации как положительно, так и отрицательно заряженных микрокапель. В режиме генерации положительно заряженных микрокапель в качестве распыляемого раствора использовали подкисленный ацетонитрил; в режиме генерации отрицательно заряженных микрокапель использовали чистый ацетонитрил. В обоих случаях был получен стабильный режим электрораспыления в широком диапазоне напряжения распыления U (от 2,2 кВ до 5 кВ), расстояния от капилляра распыления до поверхности жидкого электрода L (от 3 мм до 23 мм) и скорости подачи распыляемого раствора Q (от 25 мкл/мин до 200 мкл/мин). На примере реакции фенилгидразина с анисовым альдегидом было показано, что продукты реакций, протекающих в заряженных микрокаплях, и исходные реагирующие вещества накапливаются в объеме жидкого электрода.

Ключевые слова: заряженные микрокапли, электрораспылительная ионизация, реакции конденсации, жидкий электрод, масс-спектрометрия, высокоэффективная жидкостная хроматография

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Introduction

To date, a new direction in chemistry known as microdroplet chemistry which involves carrying out chemical reactions in micro- and nanodroplets generated by various methods, has been formed and is actively developing [1]. One of the most promising approaches to this synthesis method is to carry out chemical reactions in micro- and nanodroplets of an electrospray torch. In the course of mass spectrometric experiments, it was found that both simple and complex multi-stage chemical reactions can take place in micro- and nanodroplets of an electrospray torch, sometimes with a significant acceleration compared to their occurrence in the bulk phase [2]. Reactants and products of chemical reactions are collected using solid absorbers in most studies devoted to the study of chemical reactions in charged microdroplets of an electrospray torch. This approach requires a subsequent procedure for extracting the accumulated reactants and reaction products by washing the sample collector with an extractant, which is not convenient and increases time costs. A much more suitable option is the accumulation of chemical reaction products and reacting substances in a liquid sample collector. This approach will greatly simplify the further use of the accumulated reaction products for analytical and preparative purposes. In addition, the use of a suitable liquid in the liquid electrode will make it possible to realize the multiple-repeated electrospraying of reaction mixtures in a continuous mode, which in some cases should increase the yield of the reaction product. Thus, the objectives of this work were: 1) to study the fundamental possibility of electrospraying to the surface of a liquid, 2) to study the possibility of collection of reacting substances and reaction products in the volume of a liquid electrode.

Equipment and methods of HPLC-MS analysis

HPLC-MS analysis of the obtained samples was performed using a Nexera HPLC system (Shimadzu, Japan) equipped with a DGU-20A degasser, two LC-30AD chromatographic pumps, an SPD-M20A diode array detector, an LC-30AC autosampler, a CTO-20A thermostat. HPLC

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system was connected with a high-resolution mass spectrometer Orbitrap QExactive Plus (Thermo Scientific, USA) with a mass analyzer based on an orbital ion trap. Chromatographic separation was carried out on a Nucleodur PFP column (2×150 mm, 1.8 μm, Macherey-Nagel, Germany) in the gradient elution mode. Acetonitrile grade 0 (A) and water (B) with the addition of formic acid (0.1%) were used as the mobile phase. The gradient elution was set as follows: 0–1 min 20% A, then a linear gradient from 20% to 100% A from 1 to 17 minutes, keeping at 100% A from 17 to 18 minutes, then returning to the original ratios (20% A) for 1 minute and hold for 2 minutes at 20% A. The flow rate was set at 0.45 ml/min. The total analysis time was 21 minutes. The column temperature control was carried out at 40 °C. The sample injection volume was 5 μl. Ultrapure water (Type I) was used in all experiments, obtained using the Milli-Q system (Millipore, France). The high-resolution mass spectrometer system operated in the mode of detecting positively charged ions during electrospray ionization. The optimal parameters of the ion source, which ensured the maximum intensity of the mass spectra of the analytes, were used during ionization.

Experimental device

Previously, we made an experimental device [3] for studying the course of chemical reactions in micro- and nanodroplets of an electrospray torch. It used a solid absorber of reaction products, which greatly complicates their further use for preparative or analytical purposes. In this work, a modified version of the device was used. Its scheme is shown in Fig. 1. In the modernized device for collecting reaction products, a liquid electrode (LE) was proposed and implemented. The sample collector of the reaction products is a cylindrical glass cell (1) with an internal diameter of 45 mm and a height of 29.5 mm, on the bottom of which is placed a metal tantalum or copper plate, completely covering the bottom of the cell, with an electrical output, which has the Earth's potential. The cuvette is placed in a fluoroplastic cup (2) and filled with the test liquid, i.e. element (1) is actually a LE. The spray unit of the experimental device (5) consists of a spray capillary (1) made of stainless steel and having an inner diameter of 0.4 mm; walls of the main air duct (2) and capillary for gas supply (3), made of stainless steel and having an inner diameter of 0.6 mm (see Fig. 2). Electro spraying is carried out as follows: using a syringe pump (4), the solution is fed through the inlet capillary to the spray unit (5). From the end of the inner needle, the solution is electro sprayed onto the surface of the liquid electrode. The power supply (7) supplies voltage to the spray unit (6). The spraying current (on the needle) is measured with digital multimeter № 1 (8), and the current on the liquid in the sample collector is measured with multimeter № 2 (9). Changing the polarity of the voltage (Earth potential on the spray capillary, spray potential on the metal plate) makes it possible to create both positively charged and negatively charged microdroplets.

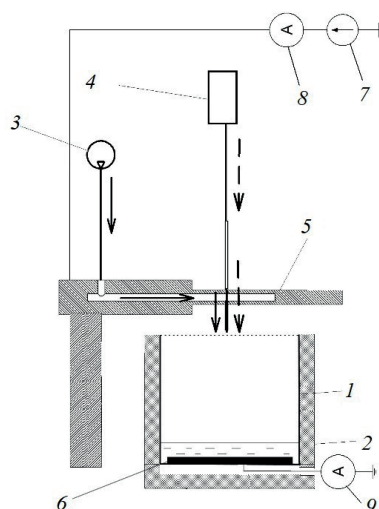


Fig. 1. 1 — glass cuvette, 2 — fluoroplastic cup, 3 — gas supply device, 4 — syringe dispenser, 5 — spray unit, 6 — metal plate, 7 — high-voltage power supply, 8 — digital multimeter № 1, 9 — digital multimeter № 2

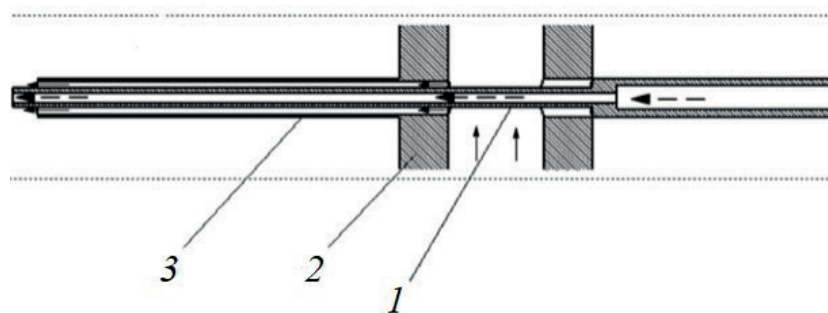


Fig. 2. 1 – spray capillary, 2 – main duct wall, 3 – capillary for gas supply

Investigation of the possibility of electro spraying to the surface of a liquid

The possibility of obtaining a stable mode of electro spraying to a liquid electrode was studied using an experimental device. For this purpose, the dependences of the electro spray current on the spraying voltage U , the distance from the spraying capillary to the surface of the liquid electrode L , and the sprayed solution feed rate Q were determined. Acetonitrile with a volume of 40 ml was used as a liquid electrode. The experiments were carried out both in the mode of positively charged microdroplets generation and in the mode of negatively charged microdroplets generation. The presence/absence of electro spraying was detected visually and with a multimeter (according to the stability of the spray current). Acidified acetonitrile was used as a spray solution in the mode of positively charged microdroplets generation. Pure acetonitrile was used in the mode of negatively charged microdroplets generation. Electro spraying was carried out without using a spray gas flow. In both cases, a stable electro spray mode was obtained. The ranges of the electro spraying potential difference, which provide a stable electro spray mode, are presented in tables 1 and 2. It should be noted that the current on the liquid electrode was equal to the electro spray current both in the mode of generating positively charged microdroplets and in the mode of generating negatively charged microdroplets in all experiments.

Investigation of the possibility of collecting reacting substances and products of chemical reactions occurring in charged microdroplets of an electro spray torch in the volume of a liquid electrode

The possibility of reaction products accumulation occurring in charged microdroplets of an electro spray torch in the volume of a liquid electrode was studied using the example of the

Table 1

Voltage ranges (in kV) that provide a stable electro spray mode for different flow rates of the sprayed solution and different distances between the spray capillary and the surface of the liquid electrode, in the mode of generating positively charged microdroplets

Sprayed solution feed rate Q , $\mu\text{l}/\text{min}$	Distance from spray electrode to liquid electrode L , mm				
	3	8	13	18	23
25	2,3 (13) – 4 (210)	3,1 (10) – 4,9 (106)	3,8(15) – 5(123)	4,2(18) – 5(95)	4,7(12) – 5(29)
50	No measurements taken	2,5(17) – 4,9(360)	3,3(22) – 4,9(171)	3,7(14) – 4,9(120)	4,4(11) – 5(56)
75		2,7(17) – 4,9(360)	3,4(14) – 4,9(174)	3,8(11) – 4,9(110)	4,4(14) – 5(78)
100		2,9(28) – 5(276)	3,6(19) – 5(168)	4,2(19) – 5(95)	4,5(21) – 5(52)
200		2,7(20) – 4,5(453)	3,3 (12) – 4,9 (229)	3,9 (16) – 4,9(124)	4,4 (12) – 5(72)

The current values in nA corresponding to the specified voltage are given in brackets.

Table 2

Voltage ranges (in kV) that provide a stable electrospray mode for different flow rates of the sprayed solution and different distances between the spray capillary and the surface of the LE, in the mode of generating negatively charged microdroplets

Sprayed solution feed rate Q , $\mu\text{l}/\text{min}$	Distance from spray electrode to liquid electrode L , mm				
	3	8	13	18	23
25	2,2 (17) – 2,9 (253)	2,8 (23) – 3,9 (186)	3,6 (23) – 5 (204)	4,3 (19) – 4,9 (90)	4,8 (18) – 5 (30)
50	No measurements taken	3,1 (16) – 3,9 (193)	3,7 (26) – 5 (180)	4,2 (16) – 5 (101)	4,6 (11) – 5 (26)
75		2,7 (11) – 4 (273)	3,5 (13) – 5 (168)	4,2 (18) – 5 (90)	4,9 (12) – 5 (23)
100		3,6 (70) – 5 (455)	4,1(45) – 5(201)	Electrospraying is absent in the voltage range from 0 to 5 kV	

The current values in nA corresponding to the specified voltage are given in brackets.

condensation reaction of phenylhydrazine with anisic aldehyde with the formation of anisaldehyde phenylhydrazone. For this, a reaction mixture was prepared. The mixture was a solution of 10 μl phenylhydrazine and 10 μl anisaldehyde in 5 ml of a 0.1% acetic acid in methanol solution. Immediately after preparation, a 200 μl aliquot of the reaction mixture was sprayed onto the liquid electrode (40 ml methanol) for 2 minutes. The electrospraying of the freshly prepared reaction mixture was carried out in the mode of positively charged microdroplets generation. Q was 100 $\mu\text{l}/\text{min}$ and U was 4.2 kV. The distance between the spray capillary and the surface of the liquid electrode L was 8 mm. A HPLC-MS analysis of the LE composition was performed immediately after electrospraying. The initial reaction mixture was kept at room temperature for 3 hours and was also subjected to HPLC-MS analysis (initial reaction mixture was preliminarily diluted 200 times with methanol). The main expected reaction product is anisaldehyde phenylhydrazone. Chromatograms for total ion current, as well as extracted chromatograms for exact masses, obtained as a result of HPLC-MS analysis, are shown in Fig. 3 and 4. In all figures, 1 is chromatogram for total ion current, 2 is extracted chromatogram for exact mass for the ion m/z 94.0652 (protonated aniline molecule); 3 is extracted chromatogram by exact mass

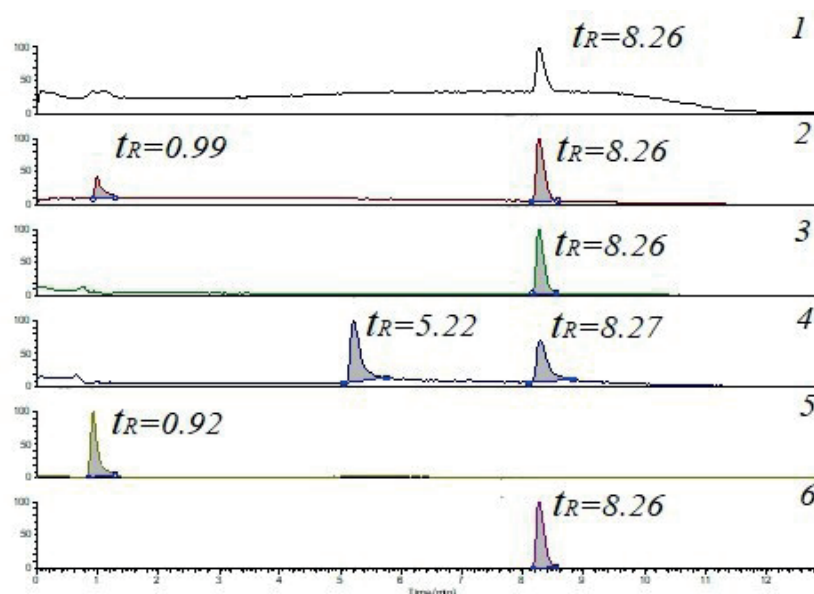


Fig. 3. Chromatograms obtained as a result of the initial reaction mixture HPLC-MS analysis

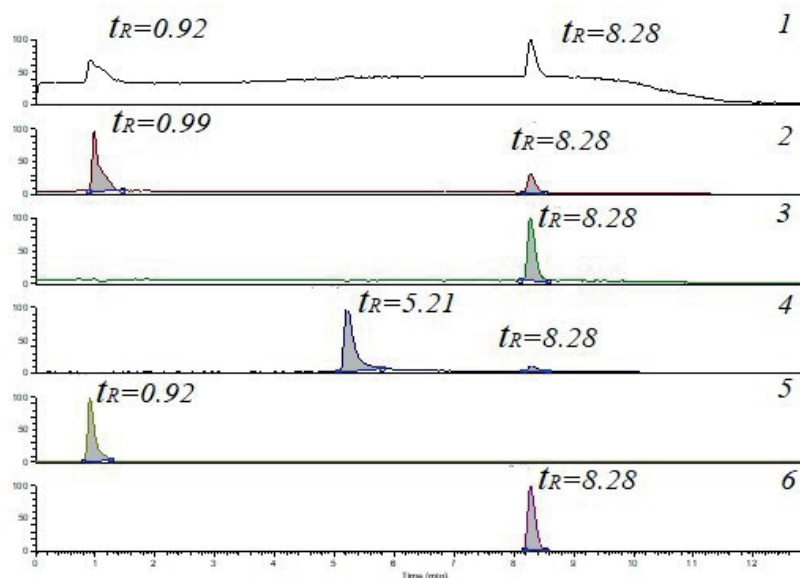


Fig. 4. Chromatograms obtained as a result of the LE HPLC-MS analysis after electro spraying the reaction mixture on it in the mode of positively charged microdroplets generation

for an ion with m/z 119.0607 (protonated 1H-indazole molecule); 4 is extracted chromatogram by exact mass for an ion with m/z 137.0603 (protonated anisaldehyde molecule); 5 is extracted chromatogram by exact mass for an ion with m/z 109.0764 (protonated phenylhydrazine molecule); 6 is extracted exact mass chromatogram for an ion with m/z 227.1181 (a protonated anisaldehyde phenylhydrazone molecule).

As can be seen from the obtained chromatograms, both the reactants phenylhydrazine ($t_R = 0.92$ min) and anisic aldehyde ($t_R = 5.21$ min) and the product of their reaction phenylhydrazone anisic aldehyde ($t_R = 8.28$ min) are accumulated in the volume of liquid electrode. The presence of chromatographic peaks with a retention time $t_R = 8.28$ min on the extracted chromatograms by exact mass for ions different from the ion with m/z 109.0764 allows us to conclude that chemical reactions occur in the ion source of the mass spectrometer with the participation of anisaldehyde phenylhydrazone, contained in the analyzed samples. As a result of these reactions, anisaldehyde (an ion with m/z 137.0603 is protonated anisaldehyde molecule), aniline (an ion with m/z 94.0652 – protonated aniline molecule) and, presumably, 1H-indazole (an ion with m/z 119.0607 is protonated 1H-indazole molecule) are formed.

Conclusion

The experimental device for carrying out chemical reactions in charged microdroplets with the accumulation of reaction products and reactants in a liquid electrode was developed. In the course of the studies carried out, the fundamental possibility of electro spraying a liquid onto the surface of a polar liquid (using acetonitrile as an example) in the modes of both positively and negatively charged microdroplets generation has been shown. In the mode of positively charged microdroplets generation, acidified acetonitrile was used as a sprayed solution; in the mode of negatively charged microdroplets generation, pure acetonitrile was used. In both cases, a stable electro spray mode was obtained over a wide range of U (from 2.2 kV to 5 kV), L (from 3 mm to 23 mm) and Q (from 25 $\mu\text{l}/\text{min}$ to 200 $\mu\text{l}/\text{min}$). It was shown on the example of the reaction of phenylhydrazine with anisic aldehyde that the products of reactions occurring in charged microdroplets, as well as the reactants, accumulate in the volume of the liquid electrode.

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