NEW APPROACH TO METAL ANALYSIS IN THE FLOW

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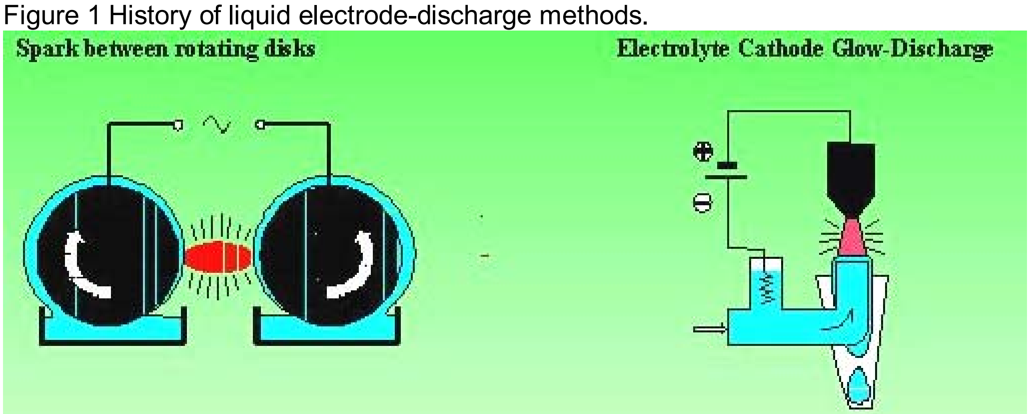
Abstract
In this work we consider a new approach to determination of elements concentration in the liquid flow in real time scale. A new atomization and excitation source for the spectrochemical analysis of electrolyte solutions is proposed. This is a discharge on boiling in a channel, which arises in a vapor gap formed in the channel of a dielectric membrane because of Joule heating. The possibility of measurements of alkali and alkaline-earth metals are studied. The results of measurements for two different applications areas are presented. There are determination of some macro components in human urine and elements migration observing in snow near highway.

Introduction
In environmental monitoring methods of express-analysis are necessary for fast detection of parameter's changes. Electrical discharges may be used in such analysis. Aqueous solutions, which are ionic conductors, are the most important test samples. Therefore, an electric discharge can be initiated directly at the surface of a test solution using the liquid as a current-carrying electrode.
Experiments with the use of electrolyte discharges in spectrochemical analysis were started more then a hundred years ago. Later, several investigations with different types of discharges were made. In the figure 1 you can see the schematic image of two devices created as the result of these experiments. One of them is an early Russian work by Dr. Rusanov and others (1). It was one of the first works where spark discharge was used for metal analysis in the electrolyte. The discharge arose between two liquid surfaces. Some portion of the electrolyte liquid is moved together with rotating disks. The second device presented here was executed by a group of Hungarian scientist (2). Here, the glow discharge between a liquid and a solid electrolyte is used. This phenomenon, which is known as an electrolyte-cathode glow discharge, is currently under study as a promising atomization and excitation source for the continuous atomic emission analysis of solutions.

Figure 1 History of liquid electrode-discharge methods.



Methods
From the very beginning our work was aimed at creating the discharge between two liquid electrodes in the flow. The work consists of two parts. One part is the Drop Spark Discharge as proposed by Dr. V.Yagov (3). The second is the discharge from Boiling in a Channel as

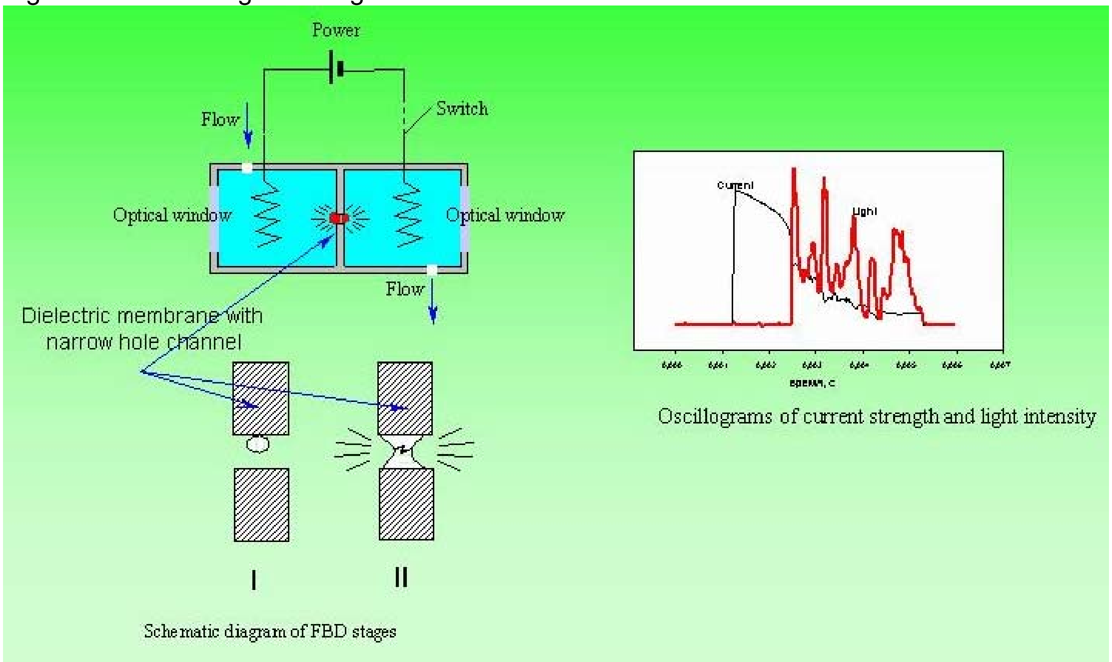
proposed by Prof. B. Zuev and Prof. B.Rudenko (4). These two approaches will be explained in more details.
Drop spark discharge (DSD) occurs after a breakdown takes place in the air gap between two approaching free electrolyte surfaces (figure 2). A discharge cell contains two glass tubes, one above the other. The analysing solution (catholyte) is delivered through the lower tube. The anolyte is added drop-by-drop from the upper tube. For the anolyte a dilute acid is used. The discharge occurs during the fall of every drop. The time interval between two drops is about 5 seconds. The emission intensity was detected in the range of 300 to 800 nm. Current and light pulses were registered by PC. On the right in the figure 2 you can see photos of the experiment taken at two different stages of discharge.

Figure 2. Drop Spark Discharge

The discharge starts when the distance between the lower surface of a drop and the upper surface of the liquid in the lower tube becomes small enough for a breakdown. The breakdown is accompanied by current and light emission pulses. In a few milliseconds the current becomes almost constant. The light intensity randomly oscillates during the whole period of discharge (stage I). Then the circuit is shorted out by an electrolyte bridge (stage II). The short leads to a drastic increase in the current and to the termination of the light emission. When at the end of the second stage the electrolyte bridge is broken, the current becomes equal to zero. The duration of the discharge is about 10^{-2} sec. During this period it is possible to register the emission spectra of metals contained in the solution.
Detection limits for a number of metals obtained by the DSD technique are from 0.1 up to 1 mg/l. Note that DSD is the method with low power consumption and therefore may be used for macro component analysis. The absence of solid/plasma interface makes it possible to avoid the memory effect. Then we should mention the reasonable reproducibility of the method. Relative standard deviation equals to 0.02-0.04.
In figure 3 you can see a schematic of the new approach. Flow boiling discharge (FBD) in a channel is a new atomization and excitation source for the spectrochemical analysis of electrolytes. A two-electrode electrochemical cell is required to start a discharge. The cell is composed of two compartments and is filled with an electrolyte solution. The compartments are separated by a dielectric membrane with a narrow hole, or channel. On closing the high-voltage circuit, the liquid in the channel comes to a boil. The current density is much higher in the channel than in other parts of the cell. A vapour bubble is formed in the channel because of Joule heating (the first stage in the diagram). Next, the channel becomes blocked by the vapour bubble, and a gas discharge appears between its liquid walls. This discharge is accompanied by a light emission. The metal emission intensity serves as an analytical signal. Oscillograms of current strength and light intensity are presented on the right in the picture. These curves show the dynamics of discharge processes.
A light-guide cable placed directly against quartz window opposite the hole was used for light emission registration. Duration of pulse was equal to 5 ms, pause between two pulses was approximately equal to 5s. The integrated light intensity averaged over three pulses was used as an analytical signal. In the figure 4, the background emission spectrum is demonstrated. It

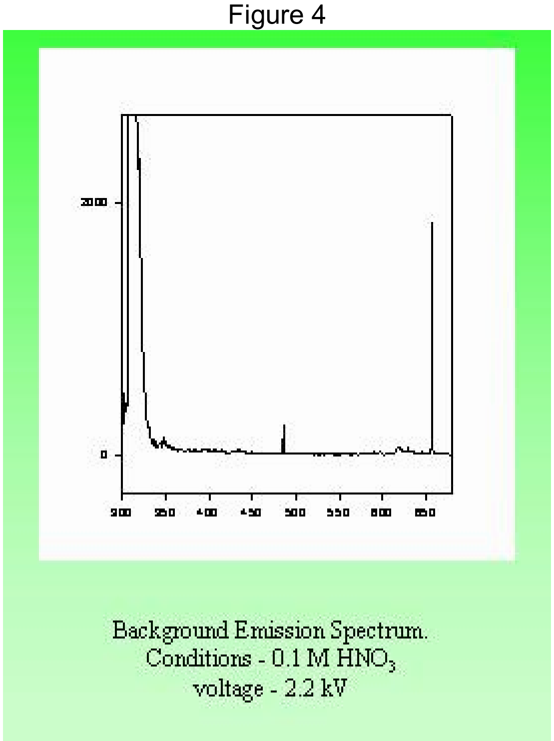
is produced by water decomposition products. Bands due to OH (306-320nm), and the Balmer series lines due to atomic hydrogen H(alpha)656, H(beta)486 and H(gamma)434

Figure 3.Flow Boiling Discharge in a Channel.



were identified in the spectrum. The major portion of the background emission energy is concentrated in the area 306-320nm.

Figure 4



Detection limits for FBD technology was 0.05 mg/l for Na, 1 mg/l for Li, 2mg/l for Ca. The rate of flow was equal to 3ml/minute.

Results

The application of the methods described above is demonstrated with two examples.

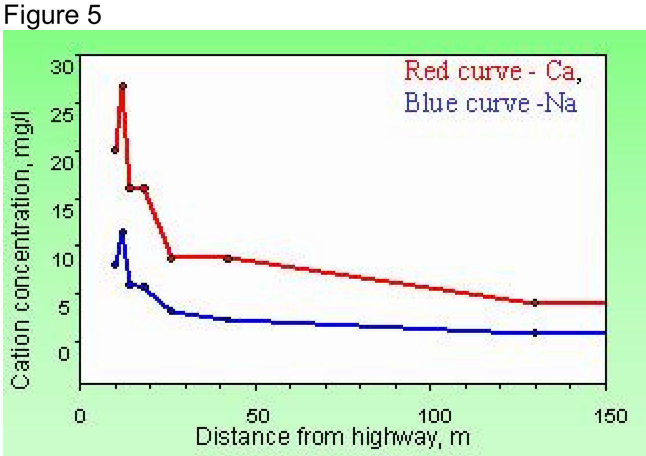
The first of them is presented in the table 1. It is an express analysis of human urine. It is well known that urine is an electrolyte, thus, it may be analyzed with the aid of our technology. We conducted the experiment with the cooperation of one of Moscow's hospitals. Seven patients were observed. In this table you can see the results of measurements of macro components in urine. You can see that concentration of some elements may significantly differ from one person to another. The relative standard deviation is about 0.05. The results were tested by independent measurements on ICP-spectrometer. In our opinion, it is possible to design an FBD-device for express analysis of macro components in human urine, which may be useful for observing the dynamics of metabolism.

Table 1: Express analysis of human urea

Element Concentration, Ppm	Patients						
	1	2	3	4	5	6	7
Ca	56	71	17	121	51	190	178
Mg	129	140	32	168	47	108	199
K	1402	2172	1119	1659	1447	1218	1664
Na	2331	5556	1611	2711	587	565	1021

The second application concerns environmental monitoring. In winter some special chemical compositions are used in Moscow to delete snow and ice from the road surfacing. Ca and Na are elements of these compositions. Our technology was used for elements migration observing in snow near highway. It allowed to predict influence of used compositions on the environment. In the figure 5 you can see a function of elements concentration depending on the distance from the highway. The data were obtained in one of Moscow forest parks (named Elk Island) traversed by the heavily travelled Moscow Ring Road.

Figure 5



Discussion

Advantages of the technology considered above are the following:

Firstly. The device works in real time. Electrolyte analysis in the flow requires several seconds only.

Secondly. The memory effect is avoided because at each step a new portion of electrolyte is involved in the discharge.

Thirdly. The measurement is easy realised in practice. No special flow of liquid with free surface should be made. The rather simple FDB device may be inserted in a tubing. Then all you need are optical window in the tubing, optical fibre and voltage.

Fourthly. The device requires low electric power (about 2W per single analysis).

And, finally, low cost and small size are the advantages too.

In our opinion, the device has a good chance in such application area as technology solutions analysis in the flow. The device is independent on gravity, so it could even be used for checking life-support systems on space crafts and stations.

Conclusions.

The new on-line method appropriate to be used for macro component analysis in the flow is proposed. The method is based on the discharge, which occurs inside the liquid between two liquid electrodes. Some examples, which demonstrate the possible areas of applications of this method are presented.

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