

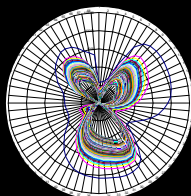
## Electrochemical analysis of multicomponent liquids



**Sergey Sokolov,**  
Ph.D. Supervisor

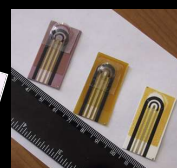
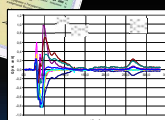
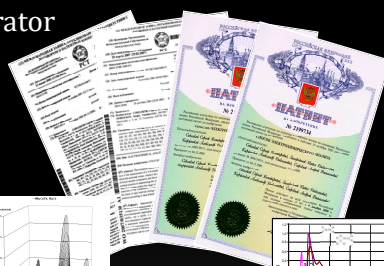
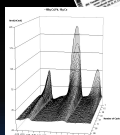


**Alexander Karzhenkov,**  
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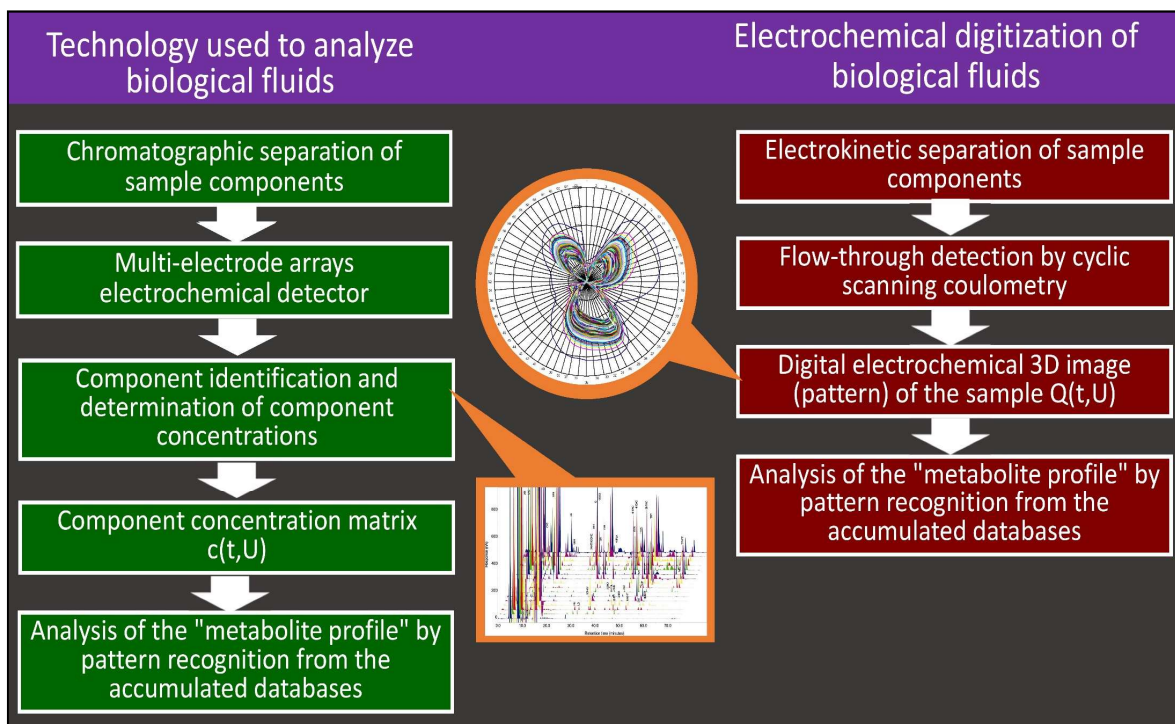


EcoSkan

**Stanislav Lyapin,**  
Lead Developer



Between 1997 and 2005, this team developed two instruments: a water analyzer for heavy metals and a flow coulometric detector for high performance liquid chromatography (HPLC) systems. Both instruments use the "scanning coulometry" method. There was one publication about the analyzer: S.V. Sokolov, P.N. Zagorodnyuk. Portable Electrochemical Analyzers. State of Art and Prospects. Russian Chemical Journal (Journal of Mendeleev Russian Chemical Society) 2001, v. XLV, №5-6, p. 80. There were no publications on the detector. For the method of electrochemical analysis of liquids received two patents of the Russian Federation.



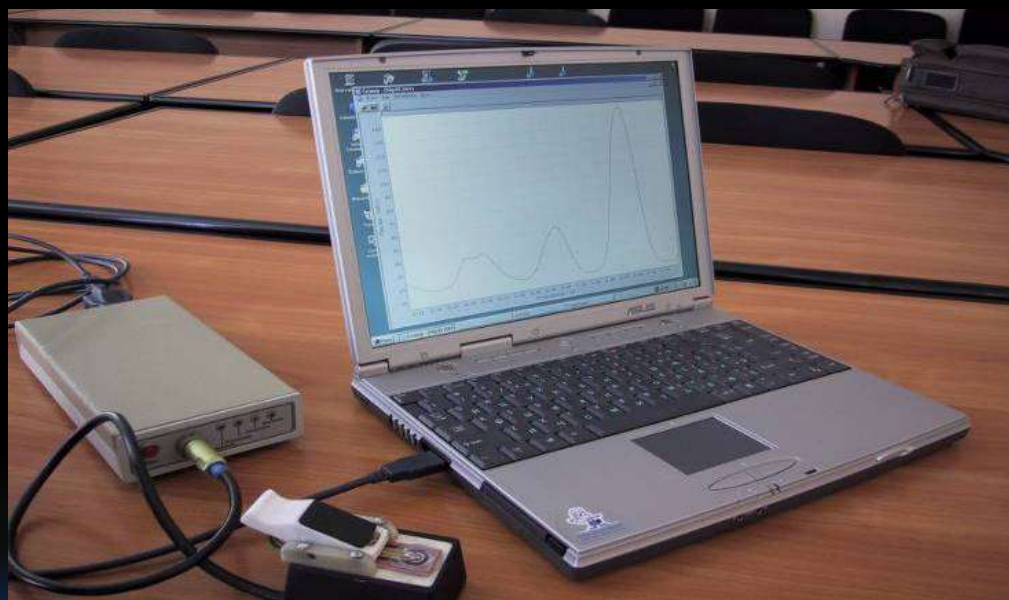
Our technology is based on a conceptually new approach that completely excludes the subjective component. That is, the experimenter cannot change in any way the initial analytical signal, which is a matrix of Faraday charges - a certain objective electrochemical image (pattern) of the sample under study, during the analysis process. This approach makes it possible to fully automate the entire analysis process. In essence, the electrochemist will not be involved in interpreting the results, transferring this function to artificial intelligence.

In our opinion, such a technology can be used in the routine analysis of biological fluid samples.

## A prototype of the ASC-2000 analyzer (2000)



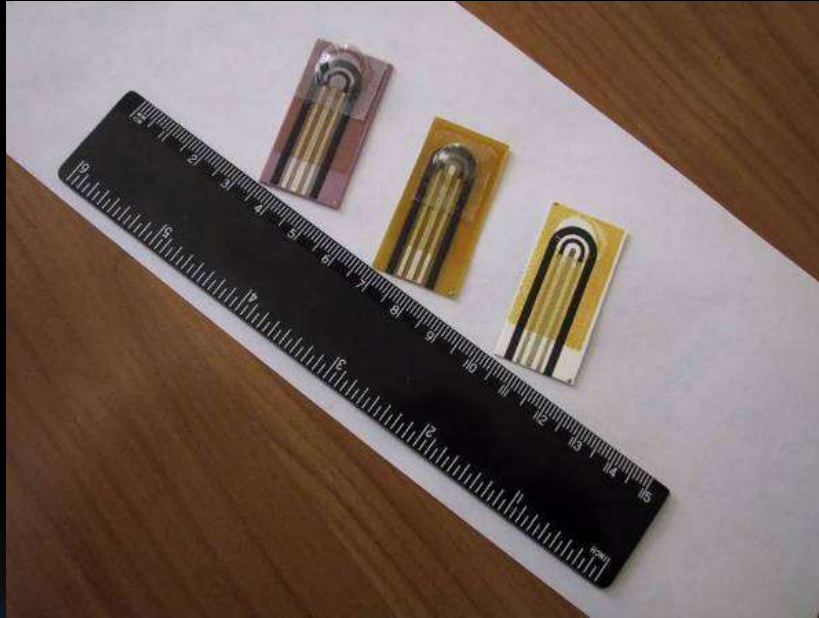
"Electrochemical tomograph" for stationary sample



ASC-2000 scanning coulometric analyzer (2000). The device actually has the ideology of a gadget (there was no such word in the lexicon yet). No controls, except for the "Reset" button, the device does not have any. Using a laptop via a wired serial interface RS-232 sets the measurement mode. After completing the measurement, the primary information, which practically does not require processing, is dumped to a computer, viewed by the operator and, if necessary, recorded in a file. The size is a bit big for a gadget, but this is a prototype. It is no bigger than a pack of cigarettes in the production version. Communication can be wireless, such as with IR ports.

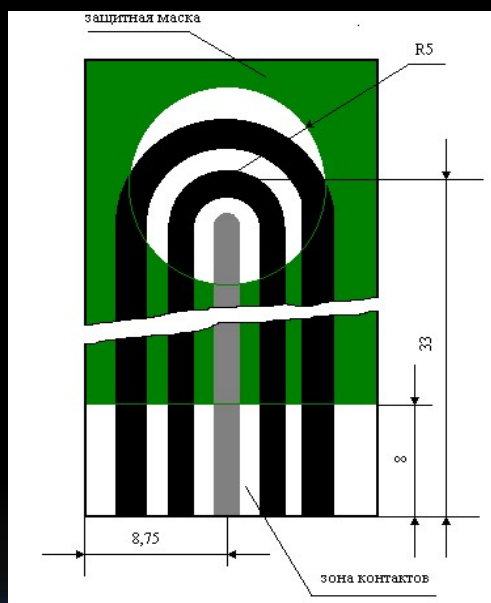
The RF patent #2199734 dated February 27, 2003, priority December 4, 2000, was received for the electrochemical analysis method. The international publication Electrochemical Analysis Method under the PCT WO 02/46736 A1 of 13.06.2002 was also issued.

## Sensors on Various Substrates (2002)

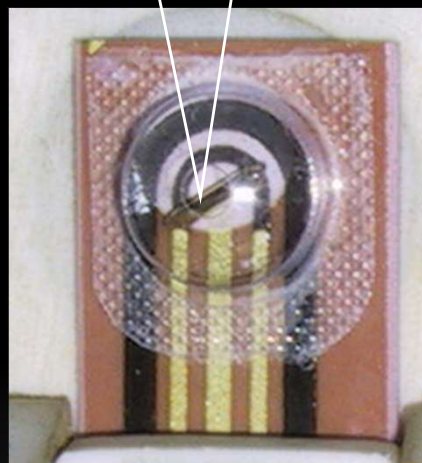


Sensors for the ASC-2000 analyzer were manufactured at a serial plant by offset lithography. Electrode material: working and auxiliary - graphite paste, reference electrode - silver paste. We made 1000 copies on different substrates: sitall, glass-textolite, radioceramics.

## Sensor, sketch and photo in a magnetic mini-stirrer

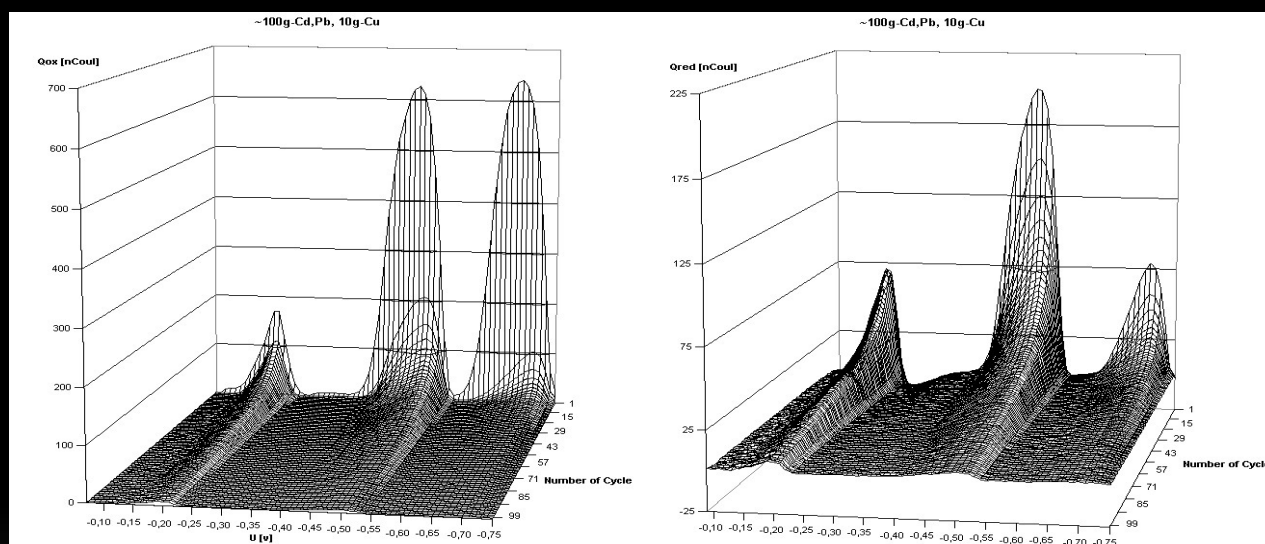


Glassed steel wire



The sensor is a three-electrode electrochemical cell with an stirrer. The working part of the sensor is closed with a PET cap with a miniature magnetic stirrer inside. A 0.125 mL sample is poured into the opening of the cap. In the photo the substrate is radioceramic.

## Analytical signal - Faraday charge matrices



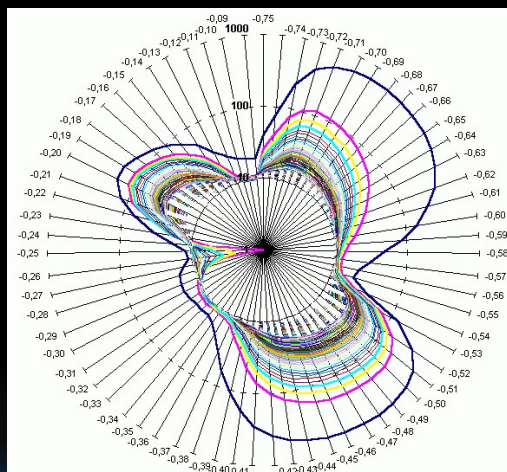
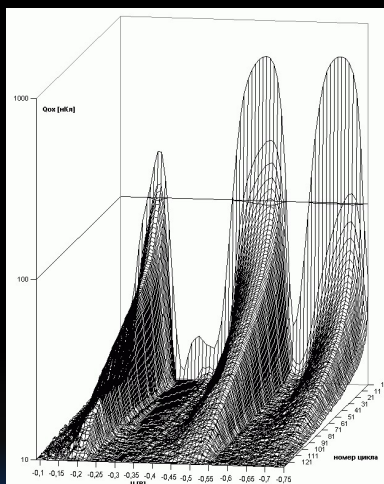
Faraday charges (nC) obtained in one measurement. On the left is the anodic process. On the right is the cathode process. Model sample: 100 ppb Cd, Pb, 10 ppb Cu.

Shown is the primary analytical signal directly from the analyzer, without any mathematical processing such as filtering (smoothing), background line subtraction, or differentiation.



## Maximum analytical information in the initial analytical volume of the signal

The analytical signal is formed by the Faraday charges of all anodic and cathodic electrochemical processes

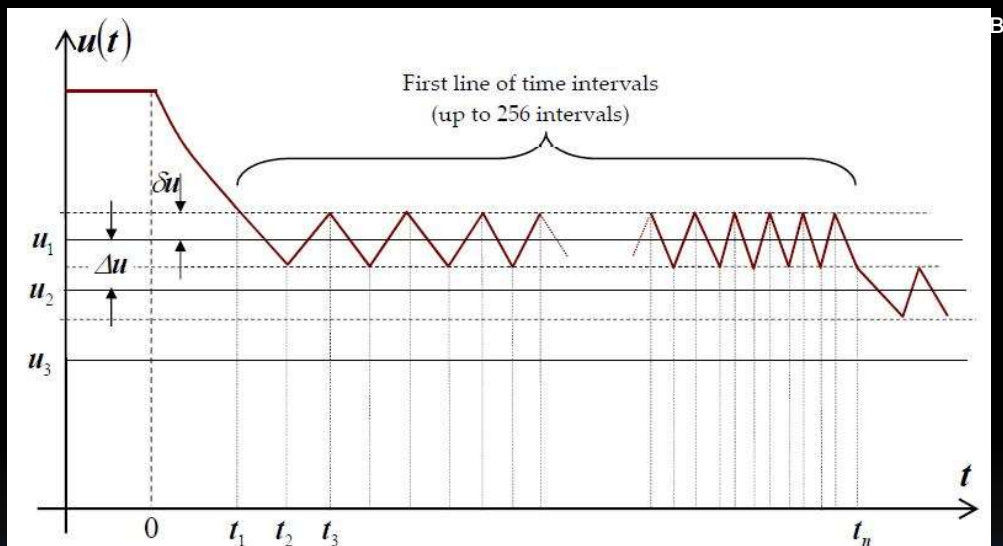


The same Faraday charge matrix in Cartesian coordinates (nC) , the anodic process, on the right - the same anodic process in polar coordinates. The scale of charges is logarithmic. Model sample: 100 ppb Cd, Pb, 10 ppb Cu.

In practically all electrochemical methods of solution analysis the analytical signal is formed from the initial, primary registered data by digital processing of this data: filtering, background line subtraction, potential differentiation by time or by conversion into the so-called "inverse derivative" of time by potential. The purpose of such processing is to extract analytically useful information. Such methods are not direct methods and require the construction of a calibration curve.

We use a direct relationship between the Faraday charges of all reactions and the number of substances that have entered into electrochemical interaction. This is a direct, reference-free measurement method based on Faraday's laws. The recorded raw signal contains comprehensive information about all electrochemical processes occurring in the sample and does not require any processing.

## Maximum analytical information with minimum signal volume



The analytical signal is devoid of redundancy inherent in other methods.

The technology does not involve recording any dependence of electrical parameters, which is what other electrochemical methods are based on. For example, in voltammetry we register the dependence of current on potential, in chronopotentiometry we register the dependence of potential on time at a given value of current. We record "time itself," i.e., the moments when an analytically significant event occurs in the sensor - at a constant value of the control current, the potential of the working electrode reaches a predetermined value.

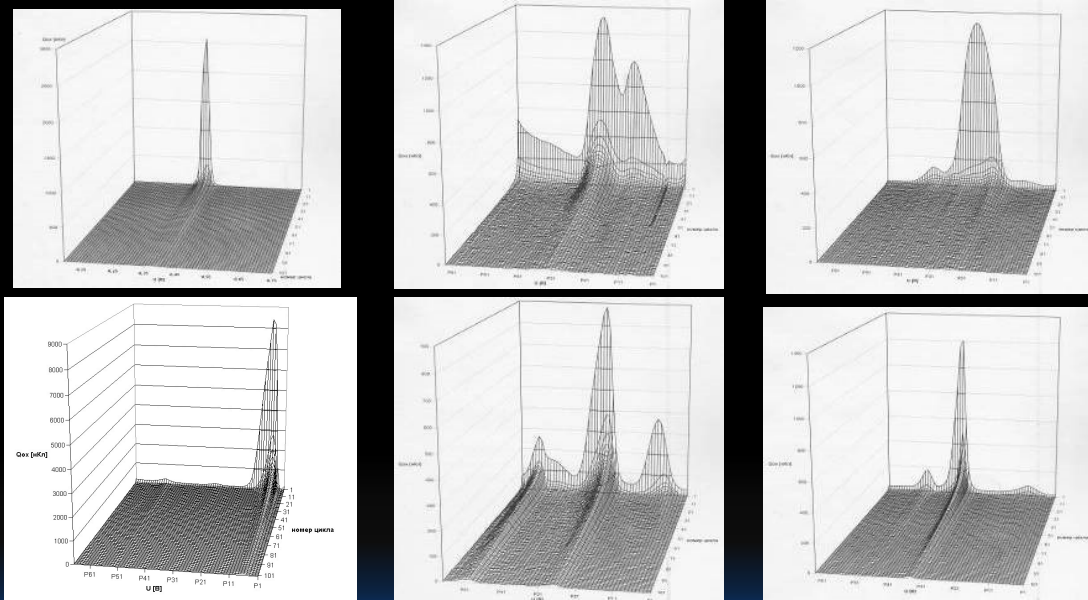
This moment is fixed and at the same time current inversion occurs that changes the direction of the process - from cathode to anode, or vice versa. And then such microcycles are repeated until differences between time intervals decrease to the preset value.

Then the next series of microcycles is repeated with new values of potentials at which the current inversion occurs.

This method of active measurement is called adaptive.



## Consistency and redundancy of analytical information



The technology makes it possible to retain the high sensitivity of measurement and large dynamic range inherent in the chronopotentiometry method. In this case, the need for digital processing of the initial signal is eliminated and its volume is significantly reduced.

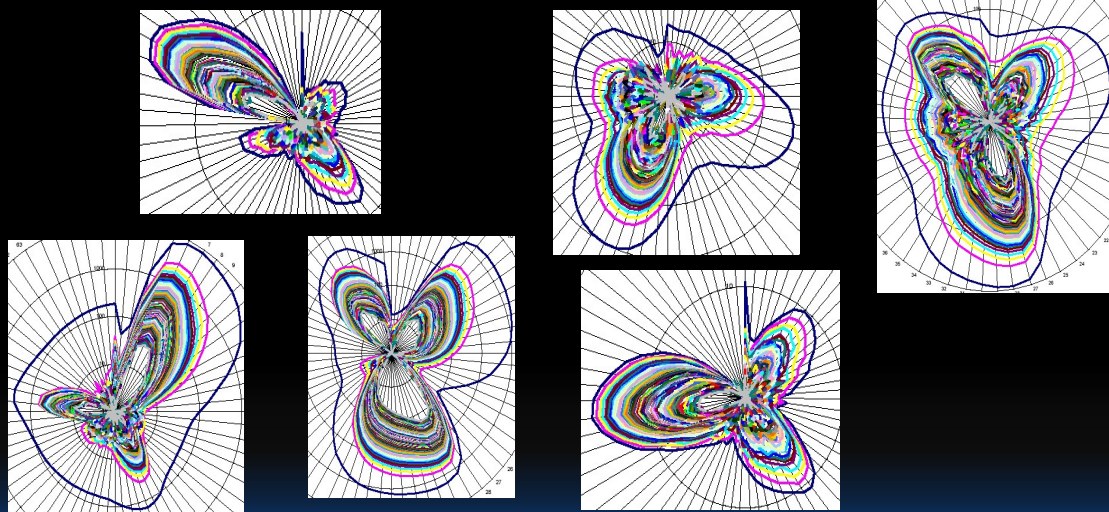
For example, at duration of measurement 3 minutes, sampling rate 250 kHz, accuracy of analog-to-digital conversion 20 bits, the volume of signal will exceed 1 Gb. At the same time, our signal will not take more than 40 Kb.

Here the analogy between digital methods of image recording is appropriate: raster (pixel) - traditional chronopotentiometry, vector - our technology.

This approach has an internal harmony (consistency) - for greater accuracy of measurement one must pay for greater duration of measurement. In measurement theory this situation is often called an analogue of the Heisenberg uncertainty principle.

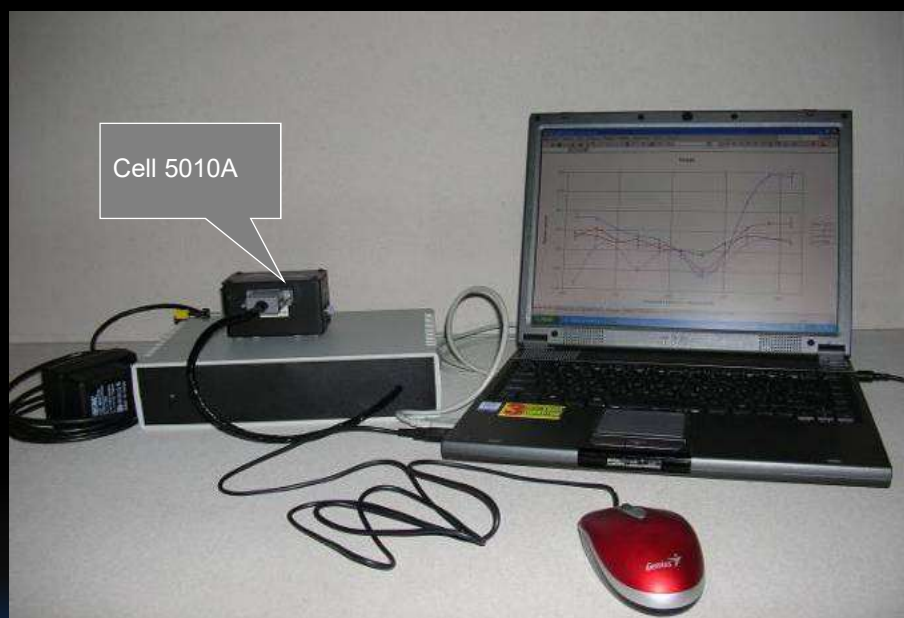
## Uniqueness of the analytical signal

The analytical signal is a unique electrochemical image (code) of a multicomponent sample



The analytical signal is formed by the Faraday charges of all anodic and cathodic electrochemical processes as well as all electrophysical and biochemical processes and is the unique electrochemical image (digital code) of the sample.

## Prototype electrochemical HPLC detector (2005)

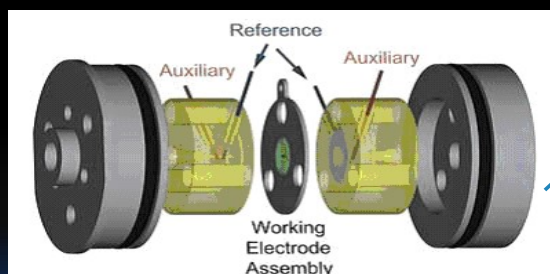
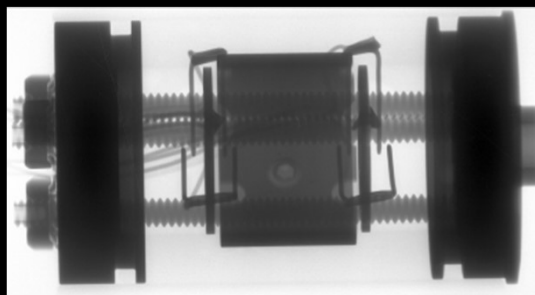
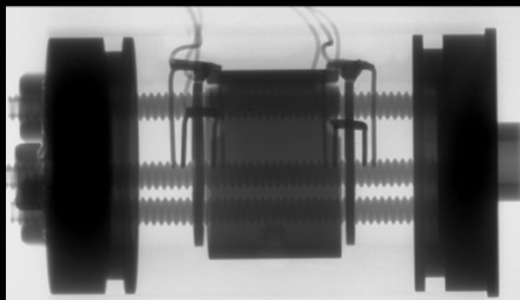


An electrochemical detector for HPLC systems, Faraday, was developed using a grant received under the program "Start-2004« (~26000USD).

The device is also based on the ideology of a gadget - it does not have any controls. The prototype of the detector is a microprocessor controller, connected via USB channel to the control computer. The sensor is a flow-through electrochemical cell commercially produced by ESA (USA). Control of the detector operation and presentation of measurement results are provided by the developed software components that use Microsoft Excel package and the FT8U245BM interface device driver for realization of the necessary functionality. The software components are executable files (DLL assemblies) for the Microsoft .NET platform.

Russian patent № 23382354 dated February 20, 2010, priority September 20, 2005 was received for the electrochemical analysis method. There was also an international publication Electrochemical Analysis Method according to PCT WO 2007/035130 A1 dated March 29, 2007. The analytical 3D signal obtained in real time contains an unprecedented amount of information about the sample under study. The device can be called "spiral scanning electrochemical tomograph" for flow-injection analysis.

## Coulometric single channel dual cell 5010A



Single cell  
construction

A dual coulometric cell from ESA Inc. 5010A P/N70-5560 S/N 5010A-0292 was used in the development. The cell has two reference electrodes and two auxiliary electrodes. Between these electrode systems are two working electrodes made of carbon material with multiple longitudinal submicron channels (microfluidic technology). Due to the large area of the channels, the conversion efficiency of the working electrode (i.e. the degree of conversion of the total charge of the ions being determined into the analytical signal) is ~99%.

The manufacturer uses the cell in coulometric mode: a current through the working electrode is measured at a fixed value of its potential.

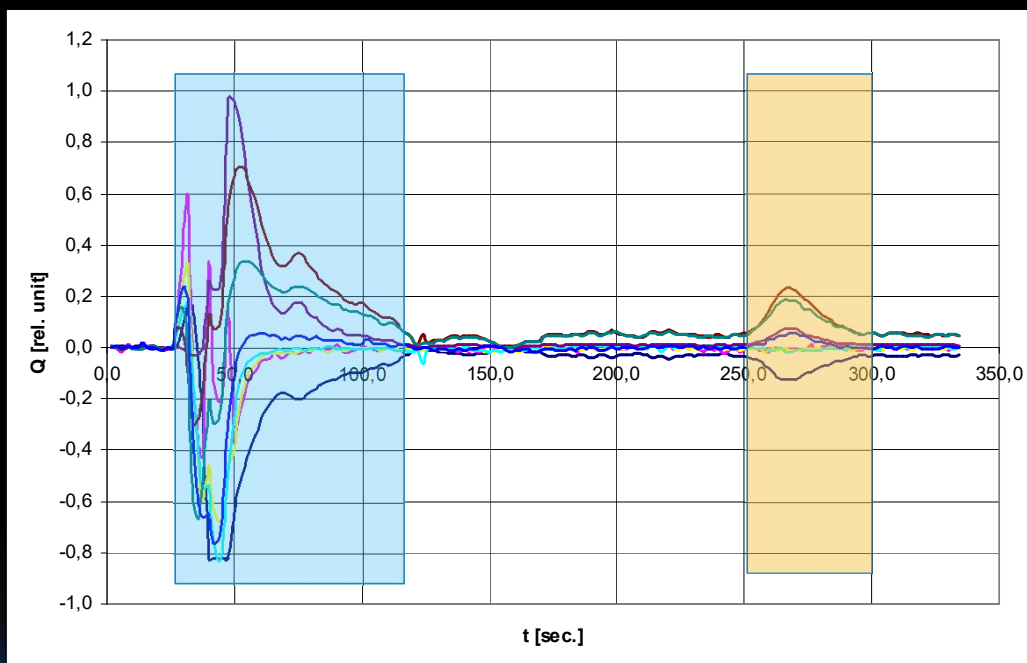
We used chronopotentiometric mode at a given current. And the measured value is the time intervals that carry information about the average rate of change in the potential of the working electrode at a given interval of potentials. At each potential interval a different value of current is set, up to the inversion of current. This ensures cyclic operation of the cell. We called such a mode as scanning cyclic coulometry (by analogy with the "scanning" mode of ASK-2000 analyzer) at a constant (for each potential interval) current.

At the top of the slide are X-ray images of the dual cell 5010A.

At the bottom is a picture of a similar cell with one working electrode (website of ESA Inc.).

In the early 2000's this company became a part of the Thermo Scientific™ Dionex™ Corporation

## Analytical detector signal in traditional form



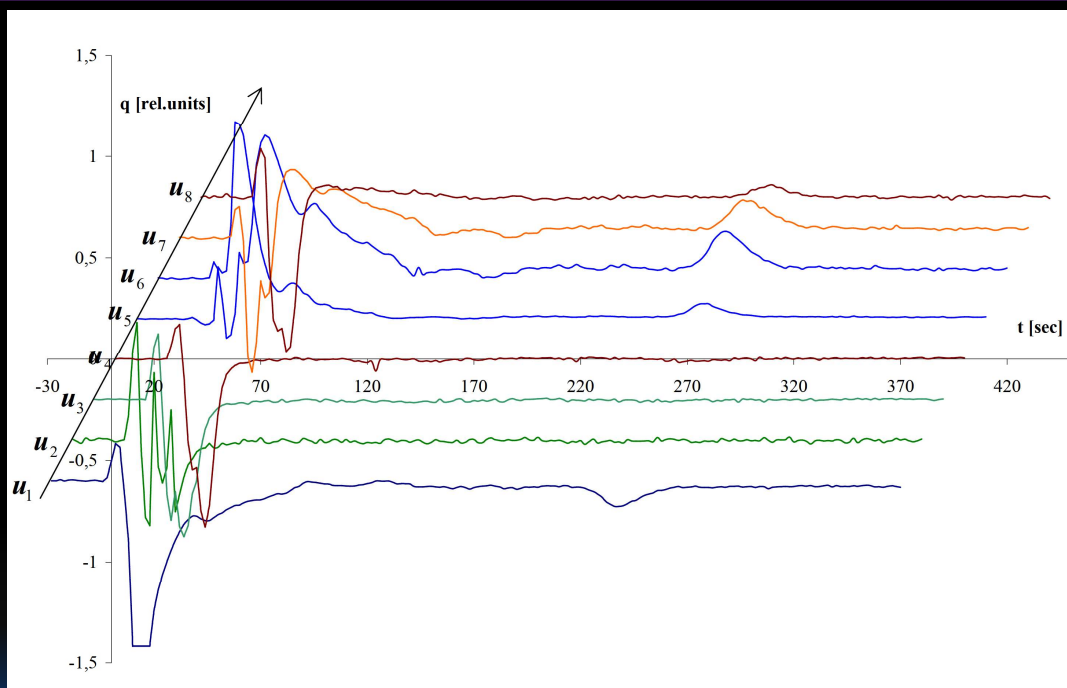
Experimental testing of the detector model was carried out in 2005 in the Analytical Center of the Faculty of Chemistry, Moscow State University (Professor O.A. Shpigun,).

The model sample contained components of liquid rocket fuel diluted in distilled water. The initial concentrations of hydrazine  $\text{N}_2\text{H}_4$ , methylhydrazine  $\text{CH}_3\text{NH-NH}$  and asymmetrical dimethylhydrazine  $(\text{CH}_3)_2\text{N-NH}_2$  (NDMH) were  $1.6 \mu\text{M}$  ( $51.2 \mu\text{g/L}$ ),  $0.16 \text{ mg/L}$  and  $0.4 \text{ mg/L}$  respectively. One of the first setup chromatograms is shown for illustration. The highlighted region in the 30-120 second range is the undivided portion of the sample, which contains an estimated 90-95 percent of the components of the liquid rocket fuel. The region of 250-300 seconds is the individual peak of one of the components of the sample, containing the remaining 5-10 percent of the component. These areas can be called dynamic electrochemical images of a mixture of rocket fuel components and one of the components.

Several chromatograms were recorded, but it was not possible to improve the selectivity of the column by adjusting the elution rate due to lack of time, because of the large load on the chromatograph.

Nevertheless, the detector reliably detected components of a model sample with a tenfold dilution, and the peak amplitude was more than an order of magnitude higher than the noise level. The concentration of hydrazine in such a sample was  $5.2 \mu\text{g/L}$ . Note that the Shimadzu electrochemical detector does not detect hydrazine in such concentrations. The threshold of hydrazine detection by the best domestic electrochemical detectors (Tsvet-Yauza chromatograph), according to the data of the leading Russian specialist in this field, A.Y. Yashin, is  $5 \mu\text{g/L}$ . Three-dimensional analytical signal of our detector, allows to receive the volume of the information at least corresponding to the firm detector with eight cells.

## Analytical signal in the form of 3D chromatogram



The same chromatogram as used to represent the results of the eight-channel coulometric detector, which uses eight flow-through electrochemical cells connected in series in the hydraulic circuit of the chromatograph.