Proceeding Paper

Sensor Device for Contactless Chemical Analysis Based on High-Frequency Inductance Coil †

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Abstract: In this work, we explore the analytical potential of a simple inexpensive sensor device based on the evolution of the high-frequency contactless conductometry method. This method was developed in the middle of the 20th century as one of the option to assess the electrical conductivity of the samples and employed electrical signal registered at a certain single AC frequency. The method did not find a wide application since the analytical signal in the developed systems was a complex function of many factors (sample conductivity, capacitive characteristics, dielectric permittivity, magnetic properties), which was difficult to be mathematically processed. We came back to this technology having the following in mind: 1) modern electronic components enable the design of such measuring devices in a very low-cost manner and allow registering the response signal in a whole range of AC frequencies; 2) application of modern machine learning tools to process these signals allows extraction of qualitative and quantitative information about the samples. It was found that the detector has numerous capabilities such as: quantification of inorganic salts in individual aqueous solutions and in complex mixtures; quantification of dielectric constants of organic solvents; distinguishing the cultures of various bacteria and cancer cells.

Keywords: electromagnetic sensor; non-contact; high-frequency; conductometry

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1. Introduction

An urgent task of modern analytical chemistry is the development of simple and inexpensive devices for the analysis of real objects in non-laboratory conditions. Such devices are in demand in chemical control of technological process, in environmental monitoring and for the detection of drugs or explosive substances. In this way, the methods that allow contactless and on-line analysis are preferred. A promising direction is the search for physical principles, initially oriented on a creation of such simple and inexpensive devices is electrical measurements. A method of high-frequency non-contact conductometry was developed in the middle of the 20th century [1]. The devices operated in the megahertz frequency region; herewith the sensor response was recorded at one particular frequency. When the electrical signal is registered in the high-frequency region, sensor response depends not only on the conductivity of the solution as in the classical conductometry. The registered electrical signal depends in a complex way on the sample conductivity, dielectric constant, magnetic properties, and capacitance in the method of high-frequency contactless conductometry. Thus, such devices were only applicable for conductometric titration, where the inductance coil was wound on a burette [2]. Due to the difficulty in interpreting the analytical signal, the method has not been widely used.

However, modern component base of electronics makes it very easy to design such devices and make them very cheap and allows registration of the analytical signal in the whole spectrum of frequencies. We have hypothesized that by processing such spectra (where the signal is registered at different frequencies of electric current) by chemometric methods, we will be able to obtain important analytical information about the sample.

2. Methods

2.1. Measuring device

We have constructed the measuring device according to the proposed methodology. The visual appearance of the sensor is shown in Figure 1. The operating principle of the detector is as follows: firstly, the signal generator produces sinusoidal alternating current in the frequency range of 2–112 MHz. Then, when a sample is introduced inside the coil, it becomes the core of the inductor, changing the properties of the electrical signal flowing through the coil. A receiver connected to the coil registers these changes, which depend on the properties of the sample (in particular on the dielectric permittivity and conductivity of the sample) and can serve as a source of information for qualitative and quantitative analysis. The coil winding shape matches the shape of the bottom of the test tube, and the signal acquisition time is less than 100 ms. All measurements were performed in 5 mL Eppendorf centrifuge conical bottom tubes with caps. The amount of sample in the tube can range from 2 to 5 mL, this is enough to ensure that the upper level of the liquid is above the upper coil winding.

More detailed information about the measurement setup and data processing can be found in [3].

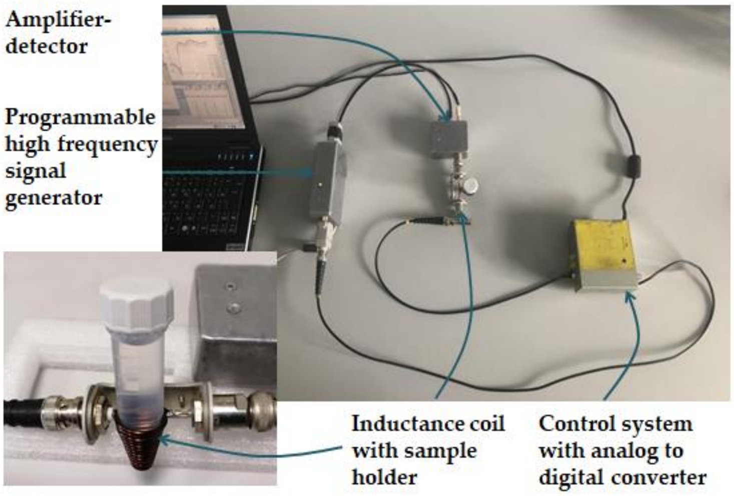


Figure 1. The visual appearance of the sensor [3].

2.2. Samples

To study the features of the proposed sensor device, different types of samples were tested: these were aqueous solutions of inorganic salts, organic solvents, complex multicomponent solutions, and the cultures of various bacteria and cancer cells.

$Ni(NO_3)_2$, KCl were procured from Sigma Aldrich (Steinheim, Germany) in pro analysis grade. NH_4NO_3, AcOH, NH_4OH were obtained from “LenReaktiv” (St. Petersburg, Russia) in highest available purity grade. Aqueous solutions of inorganic salts in 1 mol/L concentrations were prepared using weighting methods. Less concentrated solutions were prepared by sequential dilution of the parent ones. Bidistilled water was used throughout the experiments. Acetonitrile, dimethylformamide, ethanol, acetone, 1,2-dichloroethane, tetrahydrofurane, chloroform, carbon tetrachloride, toluene, benzene and hexane were obtained from JSVC Vekton (St. Petersburg, Russia) in highest available purity grade and were used without further purification [3].

The preparation procedure of complex mixtures containig NH_4NO_3, NH_4OH, AcOH was the following. The content of substances in multicomponent mixture was calculated according to the calibration mixtures design reported in [4] to ensure an absense of correlations in the content of inorganic compounds. Concentration ranges were: *C*(AcOH): 0.064- 0.216 mol/L, *C*(NH_4NO_3): 0.325 – 6.451 mol/L, *C*(NH_4OH): 0.044 – 0.548 mol/L. Nine mixtures were prepared in total; the content of inorganic compounds in these mixtures is given in Table 1. The composition of mixtures was chosen to mimic the technological solution composition in hydrometallurgical process.

The details on the real samples are provided in work [3].

Table 1. The content of inorganic compounds in complex mixtures.

Solution number	**NH_4OH (mol/L)**	**NH_4NO_3 (mol/L)**	**AcOH (mol/L)**
1	0.044	0.325	0.148
2	0.172	5.180	0.088
3	0.260	0.476	0.102
4	0.340	4.714	0.202
5	0.536	0.798	0.064
6	0.085	6.451	0.179
7	0.387	3.643	0.110
8	0.189	1.743	0.216
9	0.548	6.191	0.082

3. Results and discussion

The measurements with the described sensor device produce a spectrum for each specific sample. The figure 2 shows a general view of such a spectrum. The frequency values are plotted along the abscissa axis, and the values of the received analytical signal for each specific frequency are plotted along the ordinate axis.

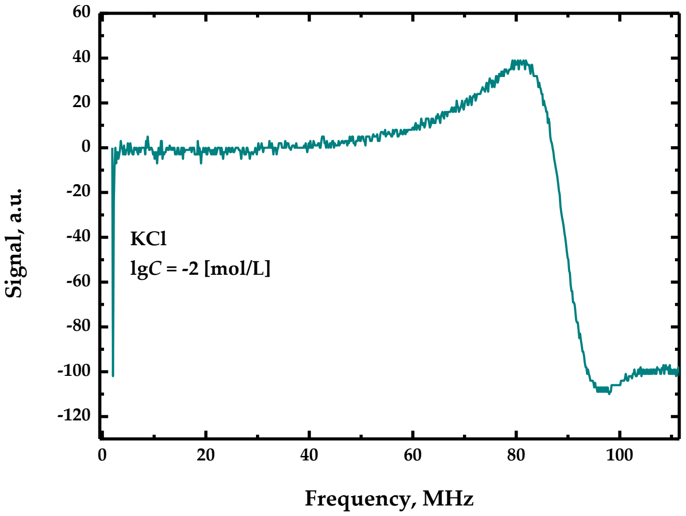
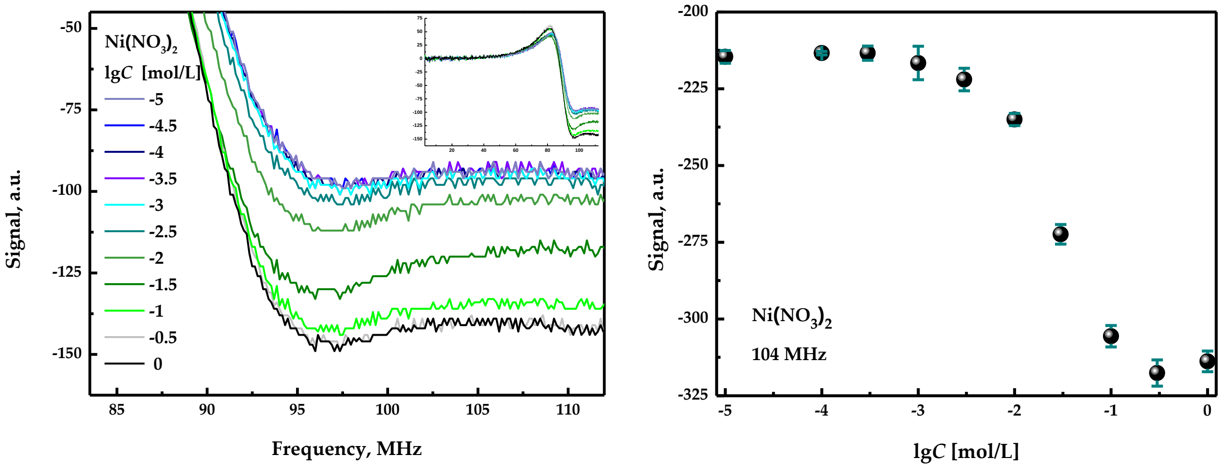


Figure 2. General view of the spectrum.

3.1. Quantification of inorganic salts

At first, the device was applied to quantification of inorganic salts in individual aqueous solutions. Figure 3a shows the full spectra for $Ni(NO_3)_2$ at different concentrations (inset in the upper right corner of the plot) and the fragments of these spectra in the frequency range from 90 to 110 MHz. All spectra are similar in shape and differ in the signal intensity depending on the salt concentration. The figure 3b shows the calibration plot obtained for nickel nitrate at the fixed signal acquisition frequency of 104 MHz. It can be seen, that detector provides for a response in a broad concentration range from approximately 10^{-3} mol/L to 10^{-1} mol/L of a selected inorganic salt. Thus, the quantification of inorganic salts is possible in this concentration range. The examples of sensitivity to other salts can be found in [3].



(**a**) (**b**)

Figure 3. (a) Response curves registered in the aqueous solution of nickel nitrate; (b) Concentration dependence. The error bars indicate standard deviation of the signals obtained in three replicated measurements.

At the next stage of the experiment complex mixtures of NH_4NO_3, NH_4OH, AcOH were analyzed, since these mixtures are of interest for analysis in technological hydrometallurgical process. Nine solutions were prepared and analyzed using the sensor. Partial least-squares regression (PLS) was employed to construct multivariate regression models for quantification of particular inorganic compounds. In brief, PLS is a method of constructing a linear multivariate calibration model to correlate the matrix of independent variables X with the matrix of dependent variable Y by accounting for significant latent variables (LVs) and maximizing the covariance between X and Y [5]. In the context of this experiment, X is the response data matrix, i.e., a matrix consisting of analytical signal values at different frequencies; Y is a column vector containing the reference values of the measured parameter – concentration of inorganic compound.

Figure 4 demonstrates the "measured vs predicted" plot for the resulting PLS model. X-axis shows the measured $C(NH_4NO_3)$ values, Y-axis - calculated or predicted by PLS model. Determination coefficient R^2 and root mean squared error of cross-validation (RMSECV) were employed as figures of merit to assess the model performance. It can be seen that R^2 was 0.89, RMSECV was 0.88 mol/L for this concentration range; this way with the developed detector we can quantify the concentration of NH_4NO_3 in the ternary mixture. Noteworthy, the PLS models for quantification of the two other components in these mixtures had unsatisfactory metrics unsuitable for practical application.

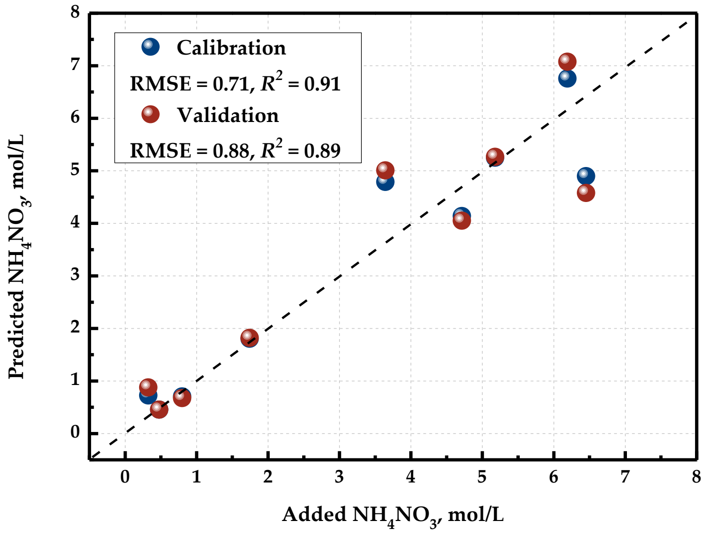
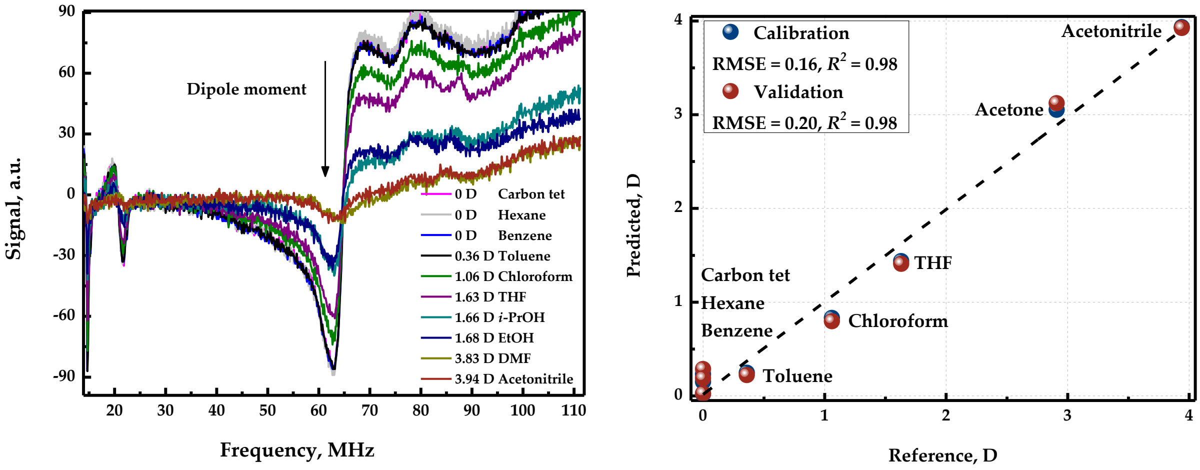


Figure 4. "Measured vs predicted" plot for PLS model predicting the concentration of NH_4NO_3.

3.2. *Analysis of organic compounds*

The figure 5a shows the spectra of various organic solvents with different dipole moments. In this case, the spectra differ both in shape and intensity, which is due to the fact that the analytical signal is influenced by dielectric permitivity, which is different for organic compounds, in addition to conductivity of the solution. Also the dipole moment of the organic compound and the observed analytical signal were found to be correlated. Figure 5b shows the "measured vs predicted" plot of the resulted cross-validated model. Therefore, applying chemometric data processing, namely by employing PLS regression, the detector can be used to estimate the polarity of unknown samples with an error of 0.2 Debye.



(**a**) (**b**)

Figure 5. (a) Response curves registered in the organic solvents with different polarity; (b) "Measured vs predicted" plot for PLS model predicting the dipole moment.

3.3. *Real sample analysis*

As a final step of this study the developed sensor was tested for analyzing real objects. It was shown that sensor can be used to quantification of integral quality parameters (fat in milk) and quantification the content of ethanol in water–ethanol mixtures in the range of 35–45% of ethanol. Also biological media containing different bacterial and cell culture can be recognized by the sensor [3].

4. Conclusion

We have proposed a new sensor device based on an inductance coil connected to a high-frequency electric field generator (1-112 MHz), which allows us to contactless registration of a signal that depends on the composition of the sample placed in the core of the coil. It is shown that the device can distinguish between samples with different physical and chemical properties.

The following advantages of the proposed principle must be pointed out: firstly, the measurement procedure is non-contact - during signal registration the sample can be placed in a plastic or glass container, which eliminates dilution or contamination of the sample; secondly, the response time of the detector is less than 100 ms, which allows real-time signal registration as well as dynamic measurements in a fluid medium; thirdly, the overall experimental layout of the device is extremely simple and inexpensive and finally no chemical reagents are required for analysis.

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