Inductive discharge as a method for direct detection of impurities in water

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Abstract. This paper reports on the excitation of atomic spectra of tap water vapor using an inductive discharge. It is shown that at a RF source frequency of 27 MHz and a plasma power output from 500 to 600 W, a steady discharge exists to pressures of $10^{-2}$ atm. Plasma temperature was determined by the Boltzmann plot method and was approximately 5500 K. At this temperature, it was possible to detect sodium ions dissolved in water. This suggests that an inductive discharge in water vapor can be used to determine the presence of impurities.

1. Introduction

There are various methods for studying materials in different states of aggregation. The systems (optical, electrochemical, thermal, magnetic) used in these methods have a complex design based on expensive elements and reagents, each system being typically designed to determine a specific substance. The high cost and complexity of these systems prevents their use for commercial and public services. Until now, control facilities have mostly used chemicals in liquid composition analysis, which limits the number of elements to be defined and require considerable time.

Emission spectral analysis is a well-established technique and is mainly used to determine the composition of metal alloys. The most common methods of emission spectral analysis are those using inductively coupled plasma [1] and flame photometry [2]. Their advantages are the possibility of quantifying the concentration of a large number (up to 50) of elements as well as the low detection limits (a few micrograms per liter). Major drawbacks of these systems are the cost, size, manufacturing complexity, and the need to use byproduct gases (argon, acetylene, oxygen). In addition, flame excitation methods are explosive, which places additional requirements on the design and operation of such plants.

On the other hand, today there is a need for rapid methods of analysis of the composition and quality of water under “field” conditions, which requires minimizing and simplifying the equipment design and reducing the time of sample preparation and analysis. Until now, water analysis in many laboratories has been carried out by chemical methods and only for several parameters: the presence of manganese, iron, pH, and bacteriological analysis. Therefore, the development and introduction of low-cost methods of analysis is an urgent task.
Previous studies [3, 4] have shown that an electrical discharge in water and at the boundary with a liquid can cause dissociation of molecules of both the liquid and the impurities dissolved therein. This makes possible qualitative and in some cases quantitative determinations of impurities, mainly metals. The main disadvantage of direct discharges between liquid electrodes in water is the low energy input into the plasma heating as most of the energy is released in the water column between the electrodes and the plasma. Furthermore, closing the electrode gap is undesirable as it leads to the appearance of the elemental composition of the electrodes in spectrum.

In this regard, we have attempted to initiate a RF inductive discharge directly in water vapor in order to develop new alternative methods of spectral analysis of aqueous media. Unlike the classical methods of spectral analysis using additional plasma-forming gases, the plasma-forming gas in our experiments was water, i.e., hydrogen-oxygen plasma. Furthermore, this type of discharge is electrodeless, which ensures the purity of the plasma.

A major issue is the method of introducing the aqueous medium into the discharge chamber. In this work, the chamber was filled with vapor as the liquid boiled out from the vessel with decreasing pressure. This is due to the need to reduce the chamber pressure because the RF source power is not sufficient for plasma ignition at atmospheric pressure. From the standpoint of detecting impurities, this method is not very good as most of the impurities, particularly heavy molecules, remain in the liquid phase and are not carried away with the vapor. However, even in this case, it was possible to record the spectrum of the light metal sodium. In the future, we plan to increase the RF source power to a level sufficient to maintain the plasma at atmospheric pressure. This will make it possible to introduce the solution directly into the discharge chamber.

2. Experimental
The discharge was excited in a quartz tube 1 of 20 mm diameter with a copper inductor having five turns (figure 1). The inductor was supplied with the 27.12 MHz frequency current from a CESAR 2710 RF source. The load power was from 500 to 600 W. A vacuum pump was placed on one side of the quartz tube, and a tap water container 2 with a metering valve 3 on the other side. The same valve 4 was placed on the side of the vacuum pump.

Before turning on the RF source, air was pumped out of the system to a pressure of ~10⁻³ atm. After that, the valve 4 was closed, and water vapor was fed to the system by means of the metering valve 3. This system made it possible to maintain the inductive discharge and perform measurements to pressures of up to ~10⁻² atm. The RF generator was then turned to initiate a discharge. The discharge spectrum was recorded from the sidewall of the quartz tube 1 through a fiber optic cable 5 with a Kolibri-2 spectrometer (VMK-Optoelektronika) having a spectral range from 190 to 1100 nm and a resolution of 0.5 nm. The discharge tube pressure was controlled by a vacuum gauge 6 (Testo 552).

![Figure 1. Schematic of the experimental setup.](image-url)
The discharge time was from 1 to 10 s. The spectrum was recorded with an exposure time of 1 s. The spectrum was then downloaded to a PC and analyzed. The distance from the end of the fiber optic cable 5 to the discharge chamber 1 was varied depending on the brightness of the recorded lines.

3. Results and analysis
In the experiments, the emission maximum was observed on the periphery near the tube wall. This indicates that the plasma temperature is maximal near the wall and, hence, the emission is virtually not absorbed by the colder layers at the wall, i.e. the resulting plasma layer can be considered optically thin.

Figure 2. Spectrum of water vapor. The abscissa is the wavelength in nm and the ordinate is in relative units. The distance from the end of the fiber cable to the quartz tube is 300 mm.

Figure 2 shows the spectrum of the inductive discharge in water vapor with a distance between the sidewall of the tube and the end of the fiber optic cable of 300 mm. The Balmer series of hydrogen and the spectra of oxygen and the OH radical are seen. The plasma temperature can be determined from the relative intensities of the Balmer series using the relative-intensity method [1]. Temperature was estimated graphically (Boltzmann plot) using the relation:

$$\ln\left(\frac{I\lambda}{A_g}\right) = -\frac{E}{kT} + C$$

where $E$ is energy of the upper (excited) level, $I$ and $\lambda$ are the intensity and wavelength of the corresponding spectral line, $A$ and $g$ are the probability of transition (in $10^8$/s) and the statistical weight of the excited level, $k$ is Boltzmann’s constant, and $C$ is a constant. The temperature can be determined as the slope of the plot in the coordinates $\ln\left(\frac{I\lambda}{A_g}\right)$ and $E$.

Figure 3 shows the plot for determining the temperature from three spectral lines of the hydrogen Balmer series and two transitions of oxygen atoms: at wavelength $\lambda = 777$ nm and $\lambda = 844$ nm using formula (1). For the hydrogen lines, the slope of the plot corresponds to a temperature of 5200 K ($kT = 1/2.24$ eV), and for oxygen lines, to 6100 K ($kT = 1/1.88$ eV). It is seen that relation (1) for hydrogen is close to linear, suggesting that the state of the plasma is close to local thermal equilibrium.
Figure 3. Boltzmann’s plot computed from (1) for hydrogen and oxygen spectral lines.

Figure 4 shows the scaled-up lines H\(\alpha\) and H\(\beta\). The points correspond to the experimentally obtained spectrum, and the solid line shows the Gaussian function approximation. According to [5], at a Stark width of hydrogen lines from 0.6 to 0.8 nm, the electron density is from \(10^{16}\) to \(10^{17}\) cm\(^{-3}\).

![Figure 4](image)

Figure 4. Profile and width of lines. (a) for H\(\alpha\) and (b) for H\(\beta\).

Figure 5 shows a portion of the discharge spectrum with a distance between the fiber optic cable and the quartz tube of 10 mm. The Na doublet line at a wavelength of 589 nm is observed. The Na concentration in the test water determined by the procedure specified by environmental regulations F14.1:2:4.167-2000 is 10 ± 1.4 mg/l.

Since water vapor enters the discharge chamber as a result of water boiling, it can be concluded that sodium ions are removed from the solution with water molecules. The sodium concentration in the water vapor was not determined. It is clear that for the entire composition of the solution to enter the plasma zone, it is necessary to optimize the method its supply. Furthermore, this problem is easily solved if the chamber pressure becomes close to the atmospheric pressure, which can be achieved by increasing the power and frequency of the inductive discharge.
4. Conclusions
The study demonstrated the possibility of initiating an inductive discharge in water vapor at pressures of up to $10^{-2}$ atm. A plasma discharge temperature from 5000 to 6000 K and a free-electron concentration in the plasma from $10^{16}$ to $10^{17}$ cm$^{-3}$ were achieved. Using the Boltzmann plot method, it was shown that the state of the plasma was close to local thermodynamic equilibrium.

The water vapor was found to contain sodium ions, indicating partial evaporation of sodium together with water as the pressure decreased.

After optimization of the method of feeding the aqueous solution into the discharge plasma, inductive discharges in water vapor can be used to determine the content of impurities with low excitation energy, e.g., alkali metals. At the same time, to determine other impurities, it is necessary to increase the plasma temperature. This requires optimizing the characteristics of the discharge chamber and increasing the power input to the inductively coupled plasma, which are the objectives of our future research.

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