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TRACE ANALYSIS BY LASER-EXCITED ATOMIC FLUORESCENCE WITH ATOMIZATION IN A PULSED PLASMA

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ABSTRACT The possibilities of plasma atomization for laser fluorescence trace analysis are discussed. Pulsed hot hollow cathode discharge was used for analysis of solutions and powdered samples. The high voltage spark and laser-induced breakdown (laser spark) were used as atomizers of metal-containing atmospheric aerosols. Detection limits were improved by means of temporal background selection.

1. INTRODUCTION

Plasma is widely used in spectrochemical emission analysis. Both sample evaporation and excitation of spectra of atoms under determination are carried out in plasma. Today ICP-AES is one of the most universal analytical techniques in the world. Glow discharge emission method (GD-AES) is widely used for the analysis of dry residues of solutions, powders and solid samples⁽¹⁻³⁾. RF GD successfully deals with non-conducting sample analysis. The laser-induced breakdown spectroscopy (LIBS) is also perspective for the aerosols-containing gases monitoring^(4,5).

However the production of high-pure substances today needs the higher sensitivity than 0.01-1 ppm level usually obtained by emission analysis. One of the ways to improve the analytical performance of the methods based on plasma atomization is to use the laser-excited atomic fluorescence. It is well known that in some cases the single atom can be detected by this technique⁽⁶⁻⁸⁾. Besides the pulsed plasma atomization is more suitable for the pulsed lasers usually used in laser fluorescence than the continuous atomization. Moreover, the pulsed plasma makes it possible to pump atoms from the excited or metastable levels for the element that could not be excited by laser radiation from the ground state directly⁽⁹⁾.

The article demonstrates the analytical possibilities of laser fluorescence with pulsed plasma atomization in the case of trace analysis of solutions, powders and aerosols.

2. PULSED HOT HOLLOW CATHODE DISCHARGE**2.1. Instrumentation and operating parameters.**

In the present experiments, the quartz water-cooled discharge tube (Fig.1) was used. The discharge circuit included stabilized high voltage d.c. power supply (up to 2 kV, up to 1.5 A) and 500 Ohm ballast resistor. The possibility was provided for pulsed operation of the hollow cathode discharge. The liquid or powdered sample was placed at the bottom of the cathode. The atomization process took place under the cathode temperature up to 1800°C (cathode current

0.6-0.8 A) after a minute's ashing at 1000°C (about 0.3 A).

The fluorescence was excited by a pulsed dye laser, pumped by YAG:Nd³⁺ laser. The spectral width of the second harmonic dye laser radiation was 0.03 nm, pulse duration 10 ns, pulse energy up to 0.02 mJ and the repetition rate 12.5 Hz. The laser beam has rectangular cross-section (3.2 mm²). The lower edge of the beam was about 3 mm above the higher edge of the hollow cathode. The fluorescence radiation was collected from the zone above the hollow cathode cavity and focused through calibrated attenuators onto the entrance slit of the monochromator. For spectral filtering of the fluorescence radiation an Cherny-Turner type monochromator (2 nm/mm), equipped with a ruled grating (1200 grooves mm⁻¹) was used. The electric signal from the PMT was measured and converted into digital data by a box-car integrator with time resolution of 4 ns.

For the determination of Co, Stokes direct line fluorescence was measured at 340.512 nm, after excitation at 304.400 nm. In the case of Ni, the fluorescence was excited at wavelength 301.914 nm and was detected at 310.155 nm. In both cases the spectral slit width of monochromator was 0.2 nm. The spectral power density of the exciting laser radiation was sufficient to saturate the selected transitions.

2.2. Results and discussion

The process of sample atomization at different hollow cathode temperatures, dependence of signal on pressure and sort of a discharge gas were investigated with the aim of choosing the optimum experimental conditions for the analysis.

Effect of cathode temperature on the fluorescence intensity is illustrated by Fig.2. It shows that signal increases with rising of the cathode temperature. However, the increase in the atomizer temperature results in a significant increase the emission radiation from the analytical zone. That is connected with temperature through the discharge current. Thus the main problem in the d.c. hot hollow cathode discharge is to reduce emission background.

The time dependence of the fluorescence of cobalt at a fixed hollow cathode temperature and for different inert gases is shown in Fig.3. The sample atomization time decreased when the discharge gas was changed from He to Ne and then to Ar. Thus at 1500°C the mechanism of atomization is two-fold: besides the thermal atomization a large role is played by cathodic sputtering. This can be easily seen for the heavier gas Ar, when cathodic sputtering is more effective than in the case of He and Ne.

Effect of gas pressure on intensities of fluorescence and emission background is shown in Fig.4. As can

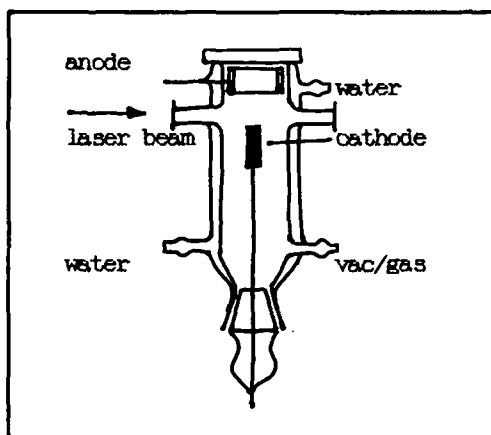


Fig.1. Discharge tube

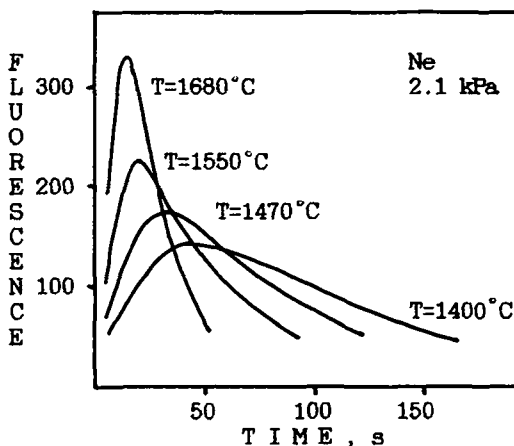


Fig.2. Temporal behavior of fluorescence at different cathode temperature

be seen the fluorescence signal increased with increasing of pressure. This is due to the increasing atomic vapour concentration near the cathode cavity resulting from an increase in the diffusion time. Furthermore, the emission background was reduced with the increase of gas pressure because the bright emitting plasma was confined into the cavity. Unfortunately, the possibility

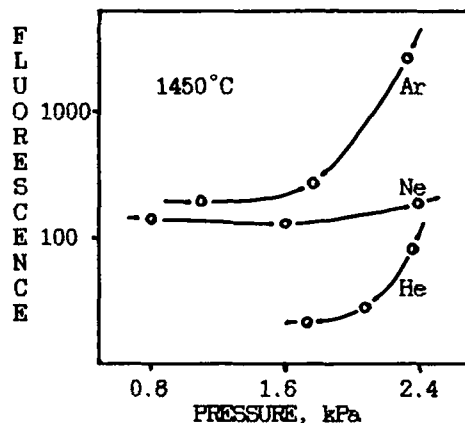
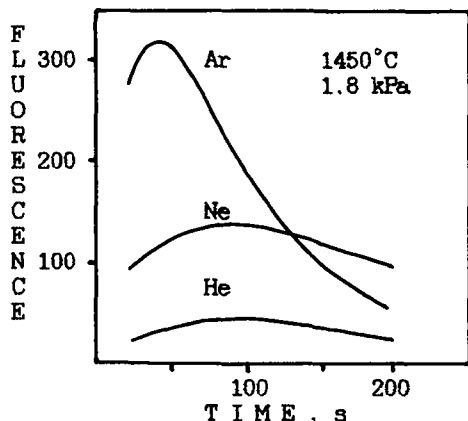


Fig. 3. Fluorescence in different gases Fig. 4. Fluorescence versus pressure

of increasing the gas pressure was limited by the stability region of the hollow cathode discharge. An arc-mode was initiated by further increase in pressure. Therefore the optimum pressure of the discharge gas is near the arc-mode regime of hot hollow cathode discharge. However it was impossible to measure low atom concentrations by operating the lamp in the direct current mode, because of the emission background of the hollow cathode plasma.

In order to improve the signal to background ratio pulsed operation of the hot hollow cathode was used. Efficient elimination of emission background was obtained by periodical switching off the discharge and exciting the fluorescence in the afterglow. This technique reduced the detection limit by 2 orders of magnitude. The pulsing of the plasma was provided by an electronic circuit synchronized with the laser pulse. It was found that the plasma was quickly ($\sim 1 \mu\text{s}$) extinguished after the discharge interruption, while the intensity of fluorescence remained constant for 300 μs . This is explained by the fact that the atomizer temperature was decreasing slowly and was practically constant at the used pulse duration.

Calibration was obtained on the basis of aqueous solutions with known Co and Ni content. To obtain the detection limit the curve was extrapolated to a value equal to three times the standard deviation of the background, determined by non-selective scattered laser radiation (wide-band luminescence of walls and windows of the discharge tube which was caused by laser radiation). Resulting LOD are: 0.02 ppb for Co in dry residues of aqueous solutions and 5 ppb for Ni in dry residues of aqueous solutions. This analytical results are comparable with laser fluorescence - ETA detection limits and better than results obtained by laser fluorescence with other atomization techniques (see review ⁽¹⁰⁾).

Determination of Co in powdered Al_2O_3 and SiO_2 was carried out with a procedure similar to that described above. Detection limits obtained are: 5 ppb for Co in Al_2O_3 and 1 ppb for Co in SiO_2 . However, optimum analytical conditions proved to be different: for Co determination in aqueous solutions, the gas (Ne) pressure was set at 2.1 kPa and the cathode temperature at 1600°C, while in the case of powders gas pressure was 1.8 kPa and the cathode temperature 1500°C. This was caused by the lower stability of the hollow cathode discharge operated with the powdered sample. For better analytical performances the stability should be improved at higher operating values of temperature and pressure.

3. SPARK PLASMA

Another type of pulsed gas discharge was used for the laser-excited fluorescence analysis of metals in air. Atomization of atmospheric aerosols was realised in the laser spark formed by focused radiation of the power laser or in the high-voltage spark discharge with very similar energy and time parameters. The main advantages of method with laser spark are:

- the possibility of analysis in real time without any sampling;
- elimination of electrode's impurities;
- high temperature that should enable high efficiency of atomization;
- high sensitivity of the analysis.

Earlier Radziemski et al (4,5) used laser-induced breakdown spectroscopy (LIBS technique) for spectrochemical analysis of metals in the air detecting the emission spectra. However in that case laser spark was used both for the sample atomization and excitation of atoms under determination. At the same time sufficient decrease of detection limits can be obtained when a spark discharge in the air is used only for aerosols evaporation, which is then followed by fluorescence detection of atoms under determination. Such an opportunity was shown in the case of analysis of Na-containing aerosols in the air.

3.1. Instrumentation and operating parameters.

Atomization of Na-containing atmospheric aerosols was carried out in the laser spark induced by focused radiation (10^{11} W/cm² power density) of the Q-switch ruby laser (20 ns pulse, up to 0.4 J/pulse, 1 Hz repetition rate) or in the high-voltage spark discharge (1 nF, 10 kV through the pulsed coaxial transformer 1:4) with very similar time and energy parameters.

Concentration of Na in the air was created by spraying aqueous solution of NaCl with Na content 10 µg/ml. The dye laser (5 ns pulse width, 0.15 mJ/pulse, 0.05 nm linewidth, up to 50 Hz repetition rate) was pumped by N₂ laser. To record resulting fluorescence monochromator with f/2.5 aperture, 2 nm/mm reciprocal linear dispersion and PMT connected with boxcar integrator (4 ns gate-width, 50 Ohm) were used.

3.2. Results and discussion

The sodium atoms fluorescence was pumped by pulsed dye laser radiation with varying time delay respectively to the spark discharge. To reduce the non-selective scattered radiation on the wavelength of registration, various components of Na yellow duplicate were used for exciting and recording the fluorescence (589.6 nm and 589.0 nm respectively). The analytical level $3^2P_{3/2}$ was populated from the level $3^2P_{1/2}$ ($\Delta E = 0.002$ eV) through collisional processes in the air.

The laser spark discharge had a continuous spectrum and relaxed during about 0.5 µs after the breakdown (Fig.5). Plasma emission of the high-voltage spark in the air had the same kinetics. At the presence of Na-containing aerosols in the analytical zone emission of Na atoms excited in the spark superimposed on the spark own glow and exceeded it in duration. Radziemski et al (4) used the differences in kinetics of plasma background and emission signal of atoms determined for decreasing of detection limit. Other possibility to reduce emission background is to excite the fluorescence in the afterglow of spark discharge. The experiment shows (Fig.6) that the maximum

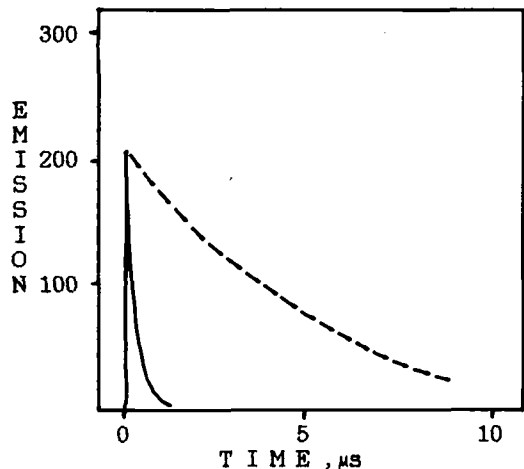


Fig.5. Kinetics of spark plasma
(- - - Na presence in the air)

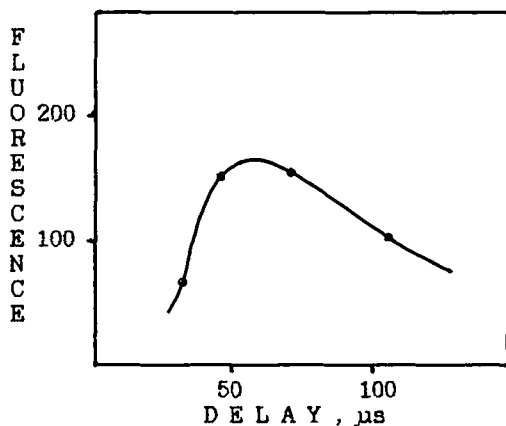


Fig. 6. Na fluorescence as a function of delay time

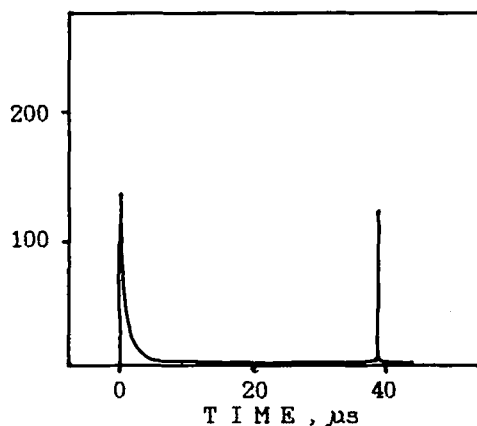


Fig. 7. Excitation of Na fluorescence (second peak) in the afterglow

of fluorescence signal was achieved at 40 μ s delay of the laser excitation from the moment of the air breakdown.

The Fig. 7 illustrates the case when concentration of Na atoms in the air is so small that the emission signal is undistinguishable against the background the plasma own glow. At the same time the fluorescence signal (the second peak) may be surely recorded that allows to conclude that lower detection limits can be obtained than those in LIBS technique.

4. CONCLUSIONS

Laser induced fluorescence in a hollow cathode discharge provides high sensitivity in the case of atomization of metals in aqueous solutions and in powdered samples. Pulsed operation allows to obtain ultralow detection limits, comparable to those reported by laser fluorescence with electrothermal atomization

It is also shown that the laser fluorescence determination of metals in aerosols with the laser spark atomization has advantages in comparison with the emission analysis.

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