Optogalvanic spectroscopy for analyzing sodium sprayed in air-acetylene sooting flames

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O Efeito Optogalvanico, uma técnica nao intrusiva e muito sensível, foi usada para estudar a concentração de íons de sódio em uma chama de gás pré-misturado vertical livre. O átomo neutro foi introduzido na chama através do sistema de nebulização de um queimador da Pelkin-Elmer, em várias concentrações. O sinal optogalvanico foi medido como função da potência do laser, da voltagem aplicada entre eletrodos e da medida de absorção da linha espectral atômica bombeada.

The Optogalvanic Effect, a very sensitive and nonintrusive technique, was used to study the concentration of sodium ions in a pre-mixed vertical free gas flame. The neutral atoms were introduced in the flame with Perkin-Elmer nebulizer system of the burner, in several different concentrations. The optogalvanic signal was measured as a function of Laser power, the voltage applied between the electrodes and the absorbance of the particular atomic spectral line pumped.

1. Introduction

The high sensitivity and simplicity of the optogalvanic detection technique[1] suggests important analytical applications and is nonintrusive. It is a powerful technique to trace element analysis in the area of flame spectroscopy. The effect of additives on soot formation in gaseous flame has been extensivelly investigated[2,3]. The alkali metals[4], the alkaline earths[5] and other metals[6] have been shown to effect the formation and behavior of soot in both premixed flat flame and diffusion flames.

The optogalvanic technique measures the rate of change of the concentration of the additives into the flame allowing to analyze locally its influence in all the stages of the mechanism of soot formation in gaseous flame. The basic concept is that if a current at constant voltage flows through the flame, the current is found to change when the flame is crossed by laser radiation tuned to an absorption line of a species seeded in the flame. This electrical signal is detected by standard measurement techniques. A synchronous detection by amplitude modulation is used to distinguish the optogalvanic effect from the continuous thermal ionization background of the flame.

The scheme employed for a given species will depend upon the energy level structure and the ionization potencial of that species[7]. For Sodium[8,9], the lower level from which Laser excitation occurs (lower transition level) is the ground level of the atom, and the excited levels are $3^2P_{1/2}(5895{,}93Å)$ or $3^2P_{3/2}(5889{,}96Å)$. A major portion of the energy required to ionize the species is provided by the photons and the final ionization step is due to collisions among the particles that are estimated to occur at a rate $> 10^9 s^{-1}$ in an analytical flame[7].

II. Experimental

The optogalvanic spectra were obtained by monitoring photon-induced current changes as a function of Laser intensity and wavelength. The set-up, shown in Figure 1, essentially consists of: 1) a tunable dye Laser,

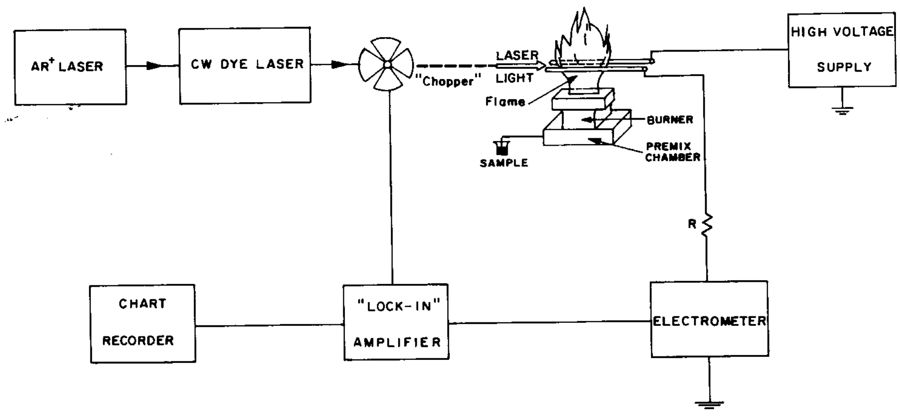

Figure 1. Set up of the experimental optogalvanic detection technique.

with $\sim$ 50mw of output power operating in the range of wavelength from 565 to 600nm as a exciting source; 2) a single slot (10cm-long) of a Perkin-Elmer standard flame spray burner, equiped with a pneumatic nebulizer which draws the sample solution from a beaker; 3) the data acquisition electronics. The electrodes consisted of two tungsten welding rods (1mm diameter), placed symmetricaly along the flame, 9mm apart, 10mm above the burner body where the optogalvanic signal was found to be stronger. The dye Laser beam was directed along the flame, close to the top of the reaction zone and exactly between the rods. Samples were prepared by dissolving Sodium Cloride in distilled water in several concentration of 0.001-10:0 mg/1 and sprayed into the air-acetylene flame at a rate of 2-3 ml/min. The flame temperature, ignoring entrainment, is estimated to be $\sim$ 2.000K. The spectra obtained were considered essentially independent of the flame stoichiometry.

The burner pneumatic nebulizer system introduces an aerosol of small droplets into the flame. The evaporation of these droplets is completed within millimeters of the flame reactor zone, rendering a portion of the analysed species from the sample in the free atomic stage.

The pulsed current induced by the chopper Laser was detected by a phase-sensitive detection and connected to a chart recorder.

III. Results and discussion

Aqueous solution of Sodium Cloride at concentrations varying from 0.001 to 10.0mg/1 were analyzed through Optogalvanic Spectroscopy, with the sodium doublet excited by dye-laser. Only one level was excited at a time. At first the current was observed in the electrometer without Laser application. Figure 2 shows the current versus the voltage applied to the tungsten welding rods (lmm diameter) electrodes, that were about 9mm apart, for concentrations of 0.5, 1.0, 2.0 and 4.0 mg/l. Figure 2 also shows the current for distilled water only. The power density (w/cm^2) of the laser radiation was kept constant and, for a given voltage, the curves show that the optogalvanic signals increase with the solution concentration. The linearity of the curves is observed for all concentrations up to about 300V applied to the electrodes and on increasing voltage further the curves tend to have asymptotic behavior, suggesting current saturation, that is more pronounced for higher concentrations. These results also reveal that, for voltages between 350 and 400V applied to the electrodes of the system, one obtains large variations in the optogalvanic signals with small concentration changes and, consequently, better precision for analysing them.

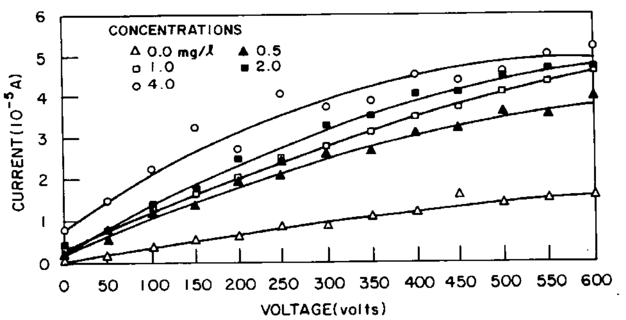

Figure 2. Current versus the voltage applied to the tungsten welding rods electrodes.

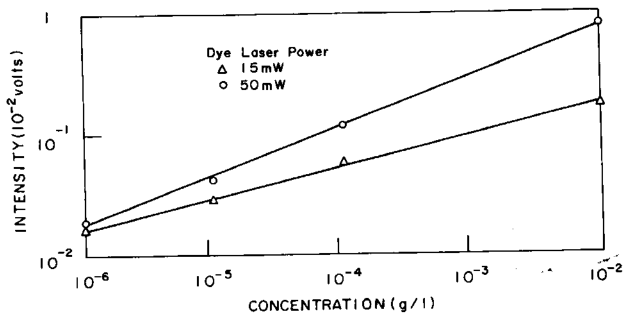

Figure 3. The optogalvanic signals versus solution concentrations relative to the sodium line 5890Å, for the 1 5mw and 50mw power of the dye laser.

The optogalvanic signals versus solution concentrations relative to the sodium line 5890Å is shown in Figure 3, for the 15mw and 50mw power of the dye Laser with the waist of lmm of the Laser beam kept constant inside the flame. A linear behavior of the curves is observed in the range of concentrations considered, and they seem to be converging to a point, where it seems to exist optical saturation and the Optogalvanic Effect independence of the incident Laser power. The figure suggests that such a point has concentrations about $0.5\mu g/1$. As it is believed that the Optogalvanic Effect is processed by collisions between of electronic excited species, at this point the electronic excitations are limited and the collisions may be monitored by changing the temperature. We believe that for this critical point and concentrations below ~ 0.5 μg/l, the relation between optogalvanic signals and solution concentration, for any power density (w/cm^2) of the Laser radiation excitation, will be linear and decreasing.

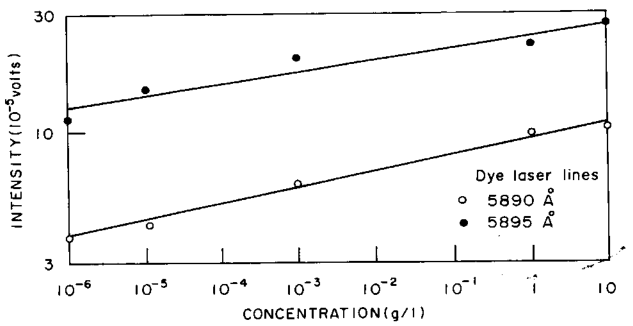

Figure 4. Intensity of the optogalvanic signal versus Sodium Chloride solution concentration for 15mw laser power ofthe lines 5890Å and 5895Å.

The transition probability for the sodium line D_2 is larger than for line D_1 and this seems to be reflected in Figure 4, where the intensity of the optogalvanic signal is shown as a function of the Sodium Cloride solution concentration for 15mw laser power for both lines. The large differences in the 5890 and 5895Å signals suggests that the cross-section differences for the transitions excited by Laser process are followed by the collisions, characteristic of the Optogalvanic Effect. This work shows that the large sensibility of the Optogalvanic Spectroscopic Technique and its very powerfull efficiency to detect very low concentrations of sodium in aqueous solutions, suggest that this technique can be used to study the mechanisms that make metals, alkali metals and alkaline earth metals inhibitors of soot formation. It also allows measuring the concentration rate of such metals in a vertical free flame as a function of height. The Optogalvanic Spectroscopy Technique, complemented with other techniques such as the extintion of a Laser bearn by the flame, for example, make it possible to analyse soot formation at each position above the reaction zone.

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