SPECTROCHIMICA ACTA

PART B: ATOMIC SPECTROSCOPY

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Evaluation of the continuous optical discharge for spectrochemical analysis*

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Abstract—The continuous optical discharge (COD) has been studied as a spectrochemical excitation source for atomic emission spectroscopy. The COD was generated by focusing a 45-W cw-CO_2 laser beam in Xe gas at pressures between 1150 and 3200 torr. The high temperature (10 000 K) and electron density ($\sim 10^{17}$ cm^{-3}) of the plasma should provide good excitation for elements difficult to excite by more conventional sources. Some characteristics of the plasma were examined as a function of laser power and gas pressure. The design of a gas cell for analytical measurements which increases plasma stability is presented. Linear calibration curves for O_2 and Cl_2 introduced into the plasma were obtained and detection limits established. Detection limits were also determined for solid materials laser ablated into the COD. Because the COD operates at pressures above atmospheric, gas samples are most easily introduced for analysis. To prevent contamination of optical components by analyte dissociation products, the COD should be operated as a plasmatron.

1. INTRODUCTION

CURRENTLY many different types of gas discharges are used to excite materials for analysis via atomic emission spectroscopy. These discharges are produced by electric fields with a range of frequencies: d.c. arcs (constant fields), a.c. arcs and sparks (1 kHz or less), the inductively coupled plasma [ICP] (20–50 MHz) and microwave induced plasmas ($\sim$ 2.5 GHz). All of these sources require some physical device to support the discharge: arcs and sparks require electrodes, the ICP uses an induction coil, and microwave plasmas employ a resonator or waveguide. Recently, however, it was hypothesized [1, 2] and then demonstrated that a free-standing continuous discharge can be produced by focusing the output of a sufficiently powerful cw-CO_2 laser in inert [3–18] and molecular [19] gases and air [20, 21] at

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atmospheric pressures or above. The discharge resides near the focus of the laser beam independent of any physical support and does not require a gas flow to stabilize the plasma, as some other sources. Because the discharge is maintained using optical frequencies (30 THz), the plasma is called a "continuous optical discharge" (COD).

A photograph of the COD produced in this laboratory is shown in Fig. 1. The plasma was small, about 1 mm in diameter, and appeared as a very bright white light. The plasma was initiated by the spark produced by a focused *Q*-switched Nd : YAG laser pulse superimposed on the focal volume of the cw-beam because the cw powers used to maintain the plasma were insufficient to induce optical breakdown. Typically, the focused powers of cw-CO_2 lasers are 10^6–10^7 W/cm^2, several orders of magnitude smaller than the 10^8–10^9 W/cm^2 breakdown threshold of atmospheric pressure gases. The pulsed laser spark plasma contains a high density of electrons ($\geqslant 10^{16}$ cm^{-3}) which act as an absorbing center for the 10.6-μm beam. The plasma can also be initiated using a conventional electrode spark [20–21] or the plasma produced on the surface of a material which is temporarily introduced into the focal volume of the cw-beam [15]. Once started, the plasma operates continuously as long as sufficient intensity is supplied to the focal volume.

The cw laser power needed to maintain the plasma depends upon the gas pressure, type of gas, and whether the cw-beam is horizontal or vertical [4]. The maintenance threshold increases with the ionization potential (I_p) of the gas [7]: at 3192 torr, powers of 59, 93, 155, and more than 480 W are needed to maintain the COD in Xe ($I_p = 12.08$ eV), Kr (13.93 eV), Ar (15.68 eV) and He (24.46 eV), respectively. About 2 kW are required to produce the plasma in air at atmospheric pressure [20, 21]. The properties of the laser beam are also important as evidenced by the widely different values for maintenance thresholds listed in the literature for identical gases and pressures [4, 10, 17]. The temperature of the COD depends upon the gas and at 1520 torr has been measured spectroscopically to be a maximum of 14 000 K in Xe,

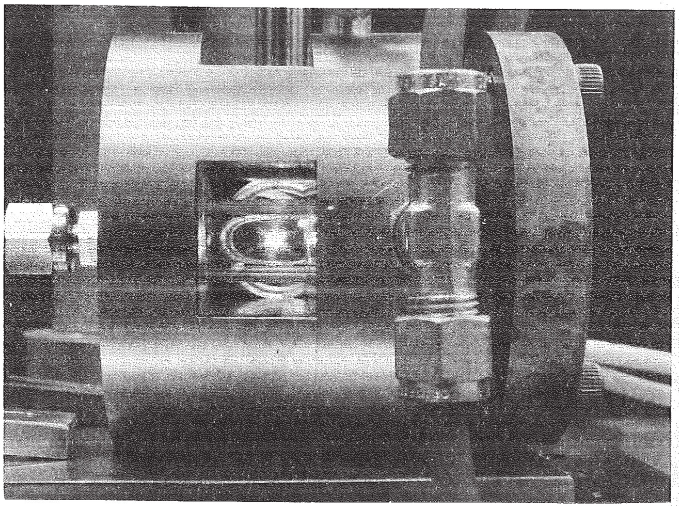

Fig. 1. Photograph of the COD produced inside a small quartz tube containing Xe at 2000 torr. The cw-CO_2 laser beam entered the cell from the right. The plasma was photographed for 1 s, at *f* 8.6, with a neutral density filter (ND) = 3 in front of the camera lens. Then the plasma was turned off and the cell photographed under room lights with the ND filter removed.

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18 000 K in Ar, and 22 000 K in N_2 [16]. These are much higher than the temperatures characterizing other continuous excitation sources: arcs (4000–5000 K), ICP (6000–8000 K) and a microwave discharge (5000–7000 K). The temperature of the COD can approach that attained by sparks (20 000 K or higher) and is due to penetration of the high frequency optical radiation into the core of the plasma [16]. At laser frequencies, which are typically above the plasma frequency [22], absorption occurs mainly via free–free transitions (inverse Bremsstrahlung) associated with electron–ion collisions [23]. For comparison, at radio and microwave frequencies, which are below the plasma frequency, plasma heating occurs through direct plasma-electric field interactions characterized by larger absorption coefficients. Consequently, only the outer layers of these plasmas are heated. The higher temperature of the COD is also related to its greater input energy density (ρ) compared to more conventional discharges. For example, for a 0.1-cm dia. plasma, a laser power of 45 W, and assuming 50% absorption by the plasma [7], $\rho = 5 \times 10^3$ W cm^{-3}, vs $\rho = 188$ W cm^{-3} for an ICP of 1.5 kW and a volume of 8 cm^3. The electron density of the Ar COD is about 10^{17} cm^{-3}, at least an order of magnitude greater than other common continuous sources [4].

Studies of the COD to date have concentrated mainly on measurements of its physical properties in various gases under different conditions. Several theoretical models of the COD have been developed to account for these properties [24–29] and a few applications have been suggested [30–32]. An almost complete listing of the previous studies is presented in the references cited herein. To our knowledge, the COD has not previously been investigated as an excitation source for atomic emission spectroscopy. The high temperatures and electron density of this plasma should provide improved excitation for species difficult to detect with cooler conventional cw sources. In addition, the COD is a single source which combines the high temperature of a spark with the continuous operation of a dc arc, the goal behind the development of many other types of spectroscopic sources [33]. In this paper we present the results of a preliminary examination of this plasma for spectrochemical analysis. Particular emphasis is placed on characteristics of COD generation, variation of plasma properties with operating parameters, and analytical performance.

2. EXPERIMENTAL

2.1. *Apparatus*

A schematic of the apparatus used to generate the COD and record the emission spectrum is shown in Fig. 2. The experimental conditions are listed in Table 1. The gas cell was evacuated to a pressure < 50 μm before adding plasma gas. The cw-CO_2 and pulsed Nd:YAG laser radiations were focused into the same volume of the cell at right angles as shown. The focal volume of the pulsed beam was adjusted to overlap that of the cw-CO_2 beam by moving the glass imaging lens slightly using an *XYZ*

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[22] The plasma frequency (ν_p) is given by $\nu_p^2 = (e^2 n_e)/(4\pi^2 \varepsilon_0 m_e)$, where e, n_e, and m_e are the electronic charge, density, and mass, respectively, and ε_0 is the vacuum permittivity. At frequencies below ν_p, EM waves interact directly with the plasma to induce heating. At frequencies above ν_p, the waves only interact with individual electrons and ions to heat the plasma. For an electron density of 8×10^{16} cm^{-3}, $\nu_p = 2.5 \times 10^{12}$ Hz, which is about an order of magnitude below the CO_2 laser frequency of 30 THz.

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