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Analysis of alcohols in an argon surface wave sustained discharge at atmospheric pressure

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Abstract

With this work, we present a study of the capacity of an argon microwave plasma generated at atmospheric pressure as an excitation and atomization source of four alcohols (methanol, ethanol, propanol and butanol). Two introduction methods for liquid samples, named *sweeping* and *bubbling* were used. The results show a great capacity of this plasma type to break the molecular bonds of these substances.

Keywords: Microwave plasmas; Analysis of alcohols; Emission spectroscopy

1. Introduction

Microwave plasmas (MIPs) sustained at atmospheric pressure, and particularly by electromagnetic surface waves (SWD), can be efficiently used as a source of atomization, excitation and ionization in atomic emission for the analytical determination of substances. Moreover, recently, these discharges have been utilized to abate greenhouse-effect gases such as perfluorinated compounds [1]. Thus, the SWDs can be considered as an effective source of reactive species used in numerous and various chemical processes, some of them being hardly carried out by the standard chemistry. The SWDs have some characteristics that offer many advantages for this type of purposes. For one, the microwave energy is coupled to the discharge using an excitation device placed out of the plasma tube, in this way long plasma columns are obtained. For another, to SWD production very low microwave powers are required, obtaining values of the electron density and temperature similar to the ones provided by other types of discharges. Moreover, the SWDs have high stability and reproducibility within a high experimental condition range. As an example of these SWD advantages we illustrate the efficient excitation of the halogens and other non-metals not readily accessible to ICP detection with inadequate sensibility [2, 3].

The main objective of this paper is to study the capacity of an argon microwave plasma generated at atmospheric pressure as an excitation and atomization source of four alcohols (methanol, ethanol, propanol and butanol).

2. Experimental procedure and results

The micro-wave induced plasma discharge was created inside a quartz tube opened at one end, with 1.5 and 4 mm of inner and outer diameters, respectively. In the case of microwave discharges, the plasma filament can be broken into two or more filaments depending on the operative conditions and the radius of the discharge tube. Kabouzi *et al.* [4] have experimentally checked that the increase of the radius favours the appearance of several filaments, but none of them is located on the axis of the discharge tube. This provides a colder plasma-free zone decreasing the fragmented molecules of the samples. The value of the inner diameter for the discharge was chosen so that the plasma occupied almost the whole cross section of the tube and, in this way, avoided this non-active plasma zone.

The gas was argon with a purity of 99,99%. The total gas flow was 0.5 slm controlled by a HI-TEC system (model IB 31). The microwave power to generate the plasma was 120 W provided by a SAIREM generator (GMP12KT/t) in a continuous mode at a frequency of 2.45 GHz. This power was supplied to generate and sustain the plasma by a surface wave launcher called *surfaguide* [5] (Figure 1).

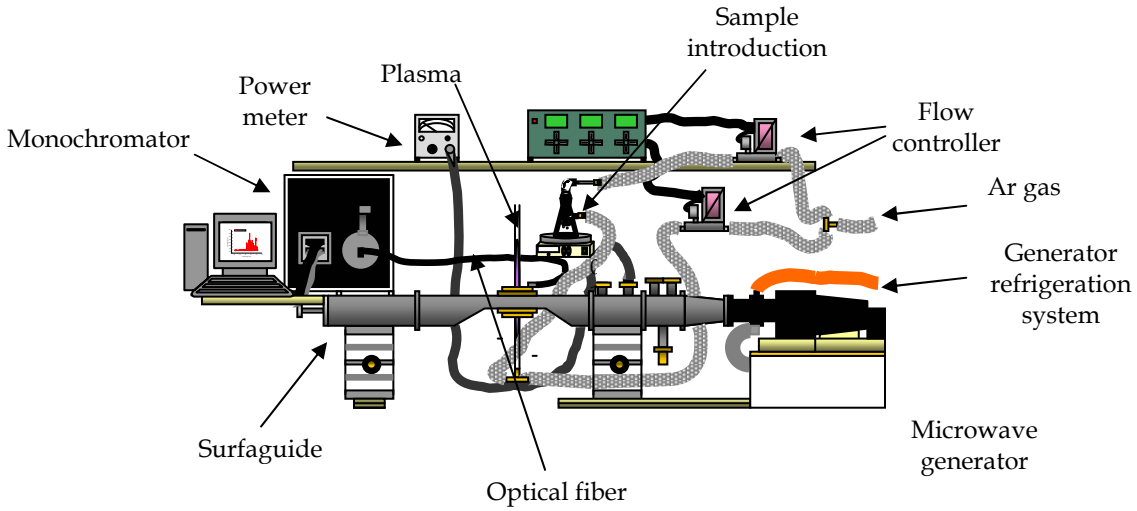

Figure 1. *Diagram of the experimental arrangement*

The different alcohol samples, methanol, ethanol, propanol and butanol, were put into the plasma using two introduction methods for liquid samples, named *sweeping* and

bubbling (Figure 2). The sample was evaporated with a slight heating in the case of *sweeping*, but not by *bubbling*. The total gas flow was divided in two parts, one of them was used as carrier gas to drag the volatile phase of the alcohol sand to be introduced into the plasma (0.14 slm). This argon flow was then united to the rest of the argon flow before introducing the total flow into the quartz tube which contains the discharge. Through the contact between argon gas and liquid alcohol the transport to the discharge is favoured. The possibility of the sample excitation processes depends on the energy available in the discharge, fundamentally in the form of the kinetic energy of the electrons and the heavy discharge particles, such as argon atoms and ions, which transmit their energy to the particles of the samples by collisions. In SWDs, the samples have to be volatilized before their introduction in the plasma, due to their low gas temperature. These sample introduction systems, above described, avoid this problem. In this way, when the alcoholic molecules are in the plasma, their bonds are more easily broken by the plasma particles, permitting the excitation of the different molecular fragments.

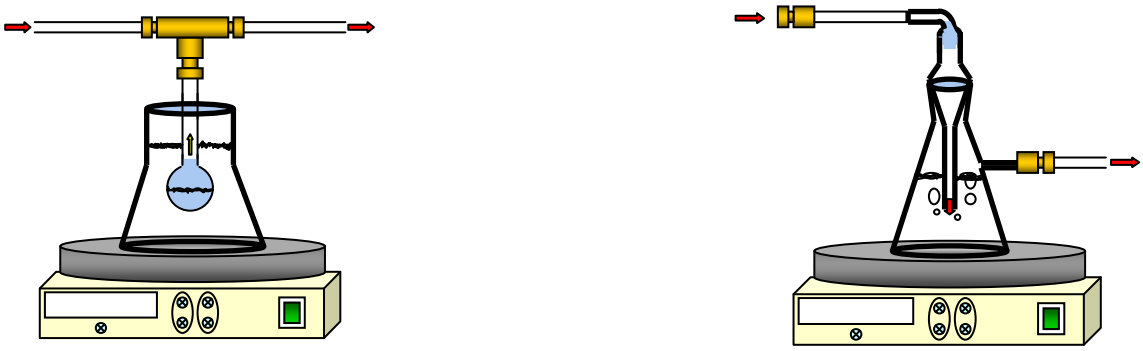

Figure 2. *Sweeping (left) and bubbling (right) sample introduction arrangements.*

The experimental data were taken from spectral lines and bands emitted by the different species in the discharge. The emission signal of the plasma was guided through an optical fibre to the entrance slit of a 1 m Jobin-Yvon Horiba monochromator. A computer-controlled CCD camera was used to register the spectra.

It was observed that, when the samples are introduced into the discharge is possible to detect rotational bands corresponding to the C_2, CN, NH, and CH species, and an increase in the hydrogen lines was also shown. This demonstrates that the bonds between carbon and hydrogen atoms in the alcohols are being broken. In addition it has been verified that all argon lines, except the 495.73 nm, decreased after sample introduction. The average electron energies on this kind of discharges are 2-3 eV and the ones of different molecular

bonds are C-C:3.6 eV, C-O:3.7 eV C-H:4.3 eV and O-H:4.7 eV. Thus, the found results show a special participation of the argon metastable atoms (11-12 eV) in the breaking of the bonds mentioned above.

From those results, we have verified that a bigger amount of the sample was introduced in the discharge when using the bubbling method was used (Figure 3), because in this case there is more contact between the carrier gas and the sample. It was observed too an increase in the rotational bands intensities being more significant for the propanol introduction. Furthermore, it was observed that, even with the sweeping method and using heating, butanol showed a lower signal on the detected bands, probably because a smaller amount of the sample was being introduced in the discharge due to the higher molecular weight.

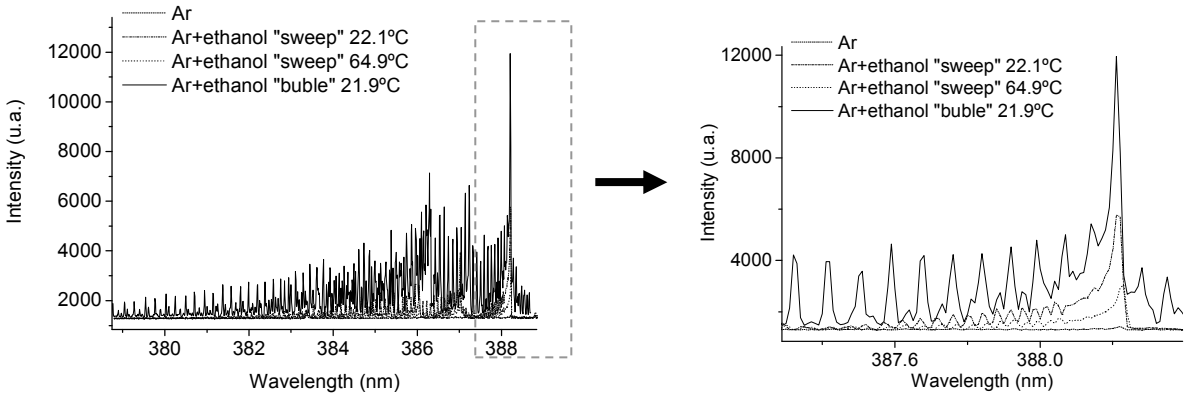

Figure 3. *CN rotational band (left) for different introduction methods and experimental conditions and detail on band head (right)*

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