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Spectroscopic determination of fundamental parameters in an argon microwave-induced plasma (surfatron) at atmospheric pressure

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Abstract—Some fundamental properties, of microwave-induced plasmas produced in a surfatron by a surface wave at a frequency of 2450 MHz and atmospheric pressure, were determined by spectroscopic techniques under various experimental conditions. These properties include electron number density and excitation, and electron and rotational temperatures. These spectroscopic diagnostics permit the characterization of departure from Local Thermodynamic Equilibrium (LTE) in this plasma.

INTRODUCTION

THE UTILIZATION of plasmas for spectrochemical excitation in atomic emission spectroscopy (AES) has increased exponentially during the last decade. The most popular spectrochemical source in AES nowadays is the inductively coupled plasma (ICP). In fact, ICP-AES has evolved into a most powerful analytical routine tool with general acceptance in industry [1].

In recent years, we have been witnessing the revival of interest in alternative plasmas to the ICP. Particularly, the study and utilization of the microwave-induced plasma (MIP) [2], whether at atmospheric pressure or at low pressures, is arousing a growing interest. The introduction of the TM₀₁₀ Beenakker cavity [3,4] and particularly the use of the surfatron, firstly proposed by MOISAN *et al.* [5,6], have played a major role in this revival of MIPs, because, though in a different way, both devices allow an efficient coupling of microwave energy to argon or helium as plasma gases. The Beenakker cavity is a resonant cavity but the surfatron is a "launcher" that permits the propagation of surface waves along the plasma column. The latter is sustained in flowing argon or helium at atmospheric or reduced pressure by the electric field of the surface wave. The principle of operation of this launcher (surfatron) has already been extensively described elsewhere [7,8].

Microwave induced plasmas produced by a surface wave with a surfatron have been widely studied during the last few years, both theoretically and experimentally, as shown by the excellent review of MOISAN and ZAKRZEWSKI [9]. The surface-wave sustained MIP is very attractive for analytical purposes because it allows a particularly stable plasma generation, being more resistant to detuning by solvent and sample loading than the more conventional resonant-cavity devices [10,11].

In a cold gas, the energy stored in the internal degrees of freedom of the atoms and molecules is a small fraction of the kinetic energy of the particles. The presence of excited and ionized states radically alters the properties of the gas that becomes a partially ionized plasma. A quantitative description of the properties of a plasma requires information about the distribution of its particles over the states of excitation. In thermodynamic equilibrium, the distribution of the particles over these states can

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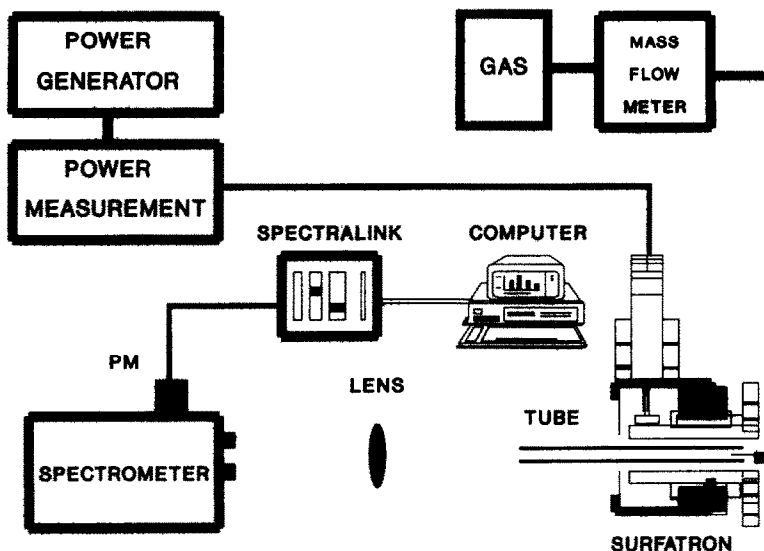


Fig. 1. Schematic drawing of the experimental set-up.

be found in an elementary way with the aid of the Boltzmann formula. Under non-equilibrium conditions, the distribution of the atoms over the levels is, in general, not characterized by a temperature and must be determined by kinetic methods. The experimental characterization of the departure from equilibrium of an MIP or ICP is usually based on the determination of temperatures by spectroscopic means. This procedure leads to the consideration of different kinds of temperature. If these are found to be different, it indicates that the plasma is far from Local Thermodynamic Equilibrium (LTE). In the experimental study of LTE departures, absolute densities represent a better experimental parameter than the temperature. Several uncertainties in temperature determinations, due to, e.g. the inaccuracy of the transition probabilities or deviations from equilibrium population densities, lead to a large scatter of temperature values. If, however, the electron density or the absolute densities of highly excited states are measured, the scatter in temperature values deduced is considerably less [12].

In recent years, different works about the physical characterization of the surfatron-MIP have been published [13–15]. Electron number density and rotational and excitation temperatures are the most common physical parameters considered in the literature [16,17]. We have set up a surfatron-MIP (Fig. 1) and report in this paper on our studies of basic properties of the surface wave plasma. Electron number density and the corresponding LTE temperature derived from the Saha equation, as well as the actual electronic excitation, electron, and rotational temperatures have been evaluated from spectroscopic measurements, as a step prior to the utilization of this surfatron-MIP in elementary analysis.

EXPERIMENTAL

Figure 1 shows a schematic drawing of the experimental set-up used. Passing through a mass flow meter, the gas supporting the discharge goes into a transparent fused silica tube, a part of which is enclosed by the surfatron. The microwave power is raised to the selected value and the surfatron tuned to obtain minimum reflected power. A Tesla coil provides the starting spark for the discharge, the plasma is “ignited” and then the system goes again to the minimum reflected power condition. The light emitted from the plasma is imaged onto the entrance slit of a monochromator (THR 1000 by Jobin–Yvon), and detected by a photomultiplier. The optical measurements are made end-on, integrating over a plasma column whose length varies with power. The measurements were carried with either slit widths of 10 or 25 μm , giving a calculated

Table 1. Operating parameters of the microwave plasma system

Microwave plasma

Generator: Microtron 200 Mark II (Electro Medical Supplies, U.K.)
 frequency: 2450 MHz \pm 25 MHz
 power: (0–200 W)
 Gas: argon (99.998%)
 Mass flow meter: Brooks R–2–25C
 i.d. of the fused silica tube = 3 mm.

Monochromator

manufacturer: Jobin–Yvon
 dispersion: 0.83 nm/mm
 focal length: 1 m
 grating: 1200 grooves/mm
 slit widths: 10/25 μ m
 photomultiplier tube: Hamamatsu R–212

bandpass of 8 and 21 μ m, respectively and a theoretical resolving power of 50000 and 19050, respectively [18]. The monochromator operation is controlled by a computer via a modular system (called Spectralink) which includes an A/D converter that directly yields the experimental data. Pre-purified argon (99.998%) from a pressurized bottle was used. The gas flows from a regulator through the thick walled tube extending through the surfatron. Typically, tubes with an inner diameter of 3 mm and outer diameter of 6 mm were used. The gas flow, as measured with a flow meter, is adjusted with a needle valve to values between 0.5 and 2 l/min. In Table 1 we give a description and specification of the major components used.

RESULTS AND DISCUSSION*Electron density*

In our studies, the electron number density was measured from Stark broadening of the hydrogen H_{β} (486.133 nm) emission line, using the H_2 impurities present in the discharge and, as a reference, we also measured the Stark broadening of the Ar I 549.587 nm [$4p(3/2)–6d(7/2)^{\circ}$]. This method does not require LTE to be reached. With the electron density measured and using Dalton's law, the charge neutrality condition and the Saha formula, we obtain, what we call, the LTE temperature, T_{LTE} . With n_e and T_{LTE} at hand, it is a straightforward matter to calculate the relative excited state population densities and relative ion and atom number densities.

The H_{β} line Stark effect is linear with the electric field intensity and inversely proportional to the square of the distance between ions ($d_{ions} \propto n_e^{-1/3}$), leading to a broadening of the line proportional to $n_e^{2/3}$. The relationship between the electron density and the full width at half-maximum (FWHM) has been calculated and tabulated by GRIEM [19,20] in the form:

$$n_e = C(n_e, T_e) \cdot (\Delta \lambda_{1/2}^{Stark})^{3/2} \quad (1)$$

where C is, for a given transition, a function of n_e and the electron temperature, T_e . In the range $5000 \text{ K} \leq T_e \leq 15000 \text{ K}$ and $2.0 \times 10^{13} \text{ cm}^{-3} \leq n_e \leq 10^{15} \text{ cm}^{-3}$, the value of C is given by $1.18 \times 10^{16} \text{ nm}^{-3/2} \text{ cm}^{-3}$ with a relative error of less than 5%. To deduce the electron number density, it is necessary to take into account both the Doppler broadening (due to the atom thermal agitation) and the instrumental broadening of the line. The recorded intensity profile of the H_{β} line is thus the convolution product of Stark $I_S(\Delta\lambda)$, Doppler $I_D(\Delta\lambda)$ and instrumental $I_{ap}(\Delta\lambda)$ profiles and we write:

$$I_{n_e}^{cal}(\Delta\lambda) = (I_D * I_S * I_{ap})(\Delta\lambda) \quad (2)$$

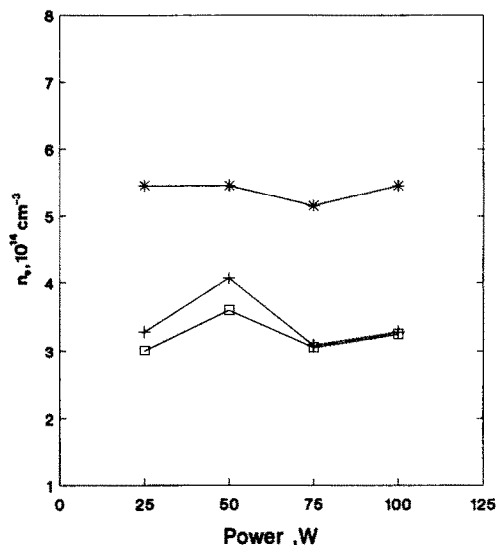


Fig. 2. Electron number density vs the net microwave power. Argon flow = 1 l/min, inner diameter of the fused silica tube = 3 mm. \square denotes the relationship between the electron density and the FWHM of the H_β emission line, + denotes a least-squares curve fitting of the H_β line to the theoretical Stark-broadened profiles and * denotes the relationship between the electron density and the FWHM of the Ar I 549.587 nm emission line.

To analyse these recordings, we used two methods, one based on the FWHM of the line and the other on its full profile. In the first case, considering the aforementioned three main causes of broadening, the total FWHM, b , is then given by [21]:

$$b \cong (d^2/4 + g_T)^{1/2} + d/2 \quad (3)$$

where d is the FWHM due to Stark broadening, and g_T is the total FWHM of the broadened profiles considered as Gaussian (Doppler and instrumental broadening, $g_T^2 = g_D^2 + g_{ap}^2$, with $g_D = 7.1 \times 10^{-7} \lambda_0 (T_g/M)^{1/2}$, where M denotes the hydrogen atomic mass, λ_0 the wavelength considered, T_g the neutral gas temperature, and g_{ap} the linear dispersion times the slit width). Since b , g_D and g_{ap} are known, $d = \Delta \lambda_{1/2}^{\text{Stark}}$ is determined and related to n_e by Eqn (1). Assuming values for T_g in the 1000–2000 K range (reasonable values in our working conditions, see later) we did not find a significant dependence of the final results on T_g . In the second method, we use a computer program to determine n_e values via least-squares curve fittings of the H_β line at 486.133 nm to the theoretical Stark-broadened profiles. The algorithm was developed and kindly made available by CHAN and MONTASER [22].

A further measurement of n_e has been performed using the Stark broadening of Ar I 549.587 nm. Its FWHM was related to the electron density via the tabulated data published by JAROSZ *et al.* [23]. In this case, we do not take into account Doppler and instrumental broadening.

Figure 2 shows the electron number density values obtained with the three methods explained above. The use of H_β -line (i.e. the relation between n_e and the FWHM and the least-squares curve fitting) gives similar results and the difference with the Ar I-line results show that the Doppler and instrumental broadening are important under our experimental conditions. We have used the n_e value deduced from the H_β line method to obtain T_{LTE} , which is in the range $7000 \leq T_{\text{LTE}} \leq 8000$ K.

Excitation temperature

Figure 3 shows a typical MIP argon spectrum, between 400.0 and 460.0 nm. The most intense lines are those corresponding to transitions between the upper excited state $5p$ and the $4s$ (3P_2) metastable state. Considering several spectral emission lines of Ar I and assuming a Boltzmann law for the distribution of the excited states, we

Table 2. Wavelengths, statistical weights, excitation energies and transition probabilities of the argon lines used for the excitation temperature measurements

λ (nm)	g	E_{exc} (cm ⁻¹)	A (10 ⁸ s ⁻¹)
425.118	3	116 660	0.00925
425.936	1	118 871	0.35080
426.629	5	117 184	0.02752
427.217	3	117 151	0.07144
430.010	5	116 999	0.02776
433.356	5	118 469	0.053425
434.517	3	118 407	0.02710

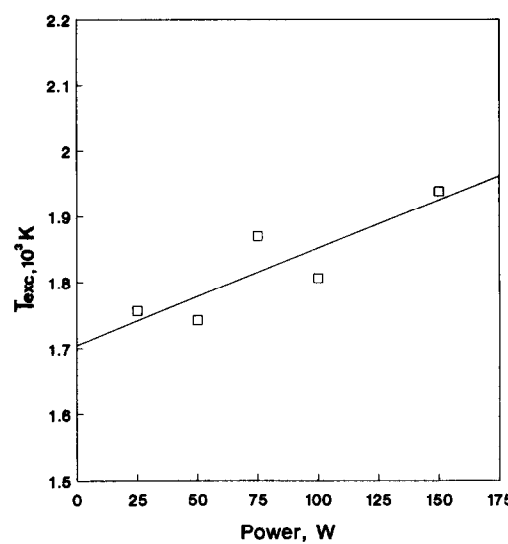


Fig. 5. Excitation temperature vs net microwave power. (Same conditions as Fig. 3.)

Electron temperature

The electron temperature was obtained using the emission spectrum of the 430.010 nm [4s(3/2)^o–5p(3/2)] argon line and the emission of the adjacent continuum. The ratio between these two intensities can be written in the form [26]:

$$\frac{I_l}{I_c} = C_r \frac{A g_i}{Q_i} \frac{1}{T_e \xi} \exp \left(\frac{E_i - E_j}{k T_e} \right) \frac{\lambda}{\Delta \lambda} \tag{5}$$

where I_l , I_c denotes the emission from the line and the continuum, respectively, g_i is the statistical weight of level j , Q_i the ionic partition function, E_i and E_j denote the energy of levels i and j , respectively, k is the Boltzmann constant, ξ a factor depending on the electron temperature, and $\Delta \lambda$ the band-pass used in the experiment. The parameters and constants that appear in Eqn (5) were taken from Ref. [26].

From Eqn (5), we can obtain T_e . Figure 6 shows the experimental values obtained. These are close to the estimated 7000–8000 K for T_{LTE} (using the experimental electron density). We believe that the use of Eqn (5) is a better experimental technique to obtain the electron temperature than the use of the Boltzmann plot, especially when the lowest excited levels are used (for lower-lying levels, the ionization/three-particle recombination balance can be disturbed by transport processes) and when the interval of E_{exc} considered is very small.

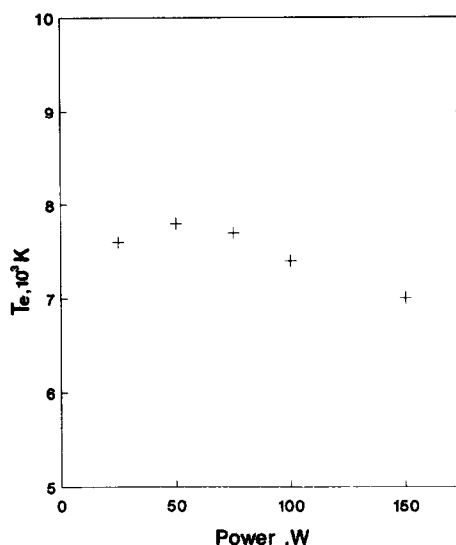


Fig. 6. Electron temperature vs microwave power. (Same conditions as Fig. 3.)

Rotational temperature

Considering the N_2^+ molecular ion and the OH radical, both present as impurities in our discharge, we have followed two different methods for the determination of the rotational temperature, assuming a Boltzmann distribution of excited states in both cases.

In the first case, we examine the so-called “first negative system” [$B^2\Sigma_u^+ - X^2\Sigma_g^+ (0, 0)$] in the 380.0–391.5 nm wavelength range and, in the second case, the [$A^2\Sigma_u^+ - X^2\Pi$] system in the 306.0–318.0 nm spectral range.

For N_2^+ , the system shows two spectral bands (*P* and *R* branches). In the case of the *R* band, the relative intensity *I* is given by:

$$\lg \left(\frac{\alpha I}{K' + K'' + 1} \right) = - \frac{2.983}{T_{\text{rot}}} [K' (K' + 1)] \quad (6)$$

with $\alpha = 1$ for the even lines and $\alpha = 2$ for the odd ones [27]. The assignment of rotational lines as a function of the quantum number K'' ($K' = K'' + 1$) is based on the works of CHILDS [28] and COSTER and BRONS [29]. Equation (6) permits us to obtain T_{rot} . Table 3 gives the characteristic parameters of the *R* band. Figure 7 shows a typical spectrum of this first negative system in our experimental conditions.

Table 3. Wavelengths and K' ($K' + 1$) values for the (0,0) band of the first negative system of N_2^+ (*R* branch) used for the rotational temperature measurements

K	λ (nm)	$(K'' + 1) (K'' + 2)$
6	390.49	56
7	390.40	72
8	390.29	90
9	390.19	110
10	390.08	132
11	389.97	156
12	389.85	182
13	389.73	210
16	389.33	306
18	389.04	380
20	388.74	462
21	388.58	506

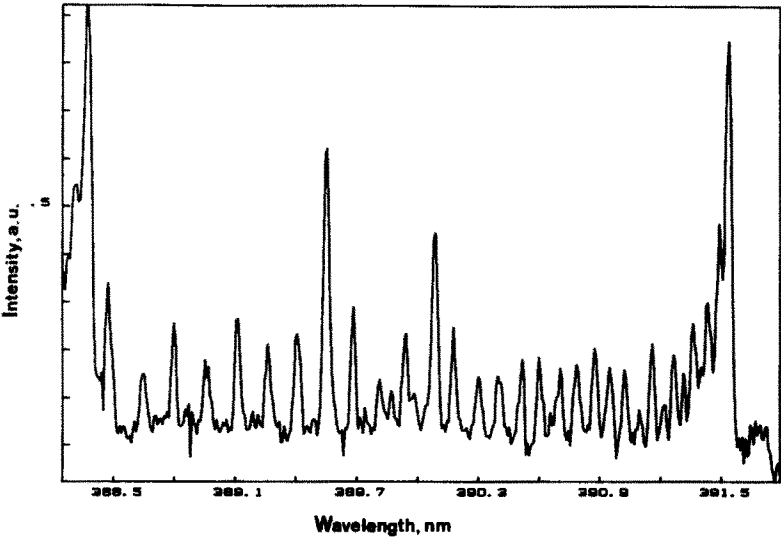


Fig. 7. Spectrum of the (0,0) band of the first negative system of N_2^+ emitted by the Ar MIP-surfatron. (Same conditions as Fig. 3.)

The Q_1 band of the OH radical spectrum is used in a similar manner to obtain a rotational temperature [27,30,31]. Table 4 gives the characteristics of this Q_1 spectral band. Figure 8 shows a typical spectrum of the OH radical under our experimental conditions.

Figure 9 shows the rotational temperature obtained using N_2^+ and OH molecules. The differences observed have already been pointed out [32] and it was stressed that it is more convenient to use N_2^+ as a thermometric probe, because the relatively strong dissociation of OH can perturb the rotational levels and thus affect the rotational temperature. We thus consider T_{rot} from N_2^+ as the gas temperature.

CONCLUSIONS

Our spectroscopic measurements on the MIP-surfatron permit us to draw the following conclusions: (a) there is a significant difference between the estimated

Table 4. Wavelengths, excitation energies and rotational transition probabilities of the Q_1 branch of OH used for the rotational temperature measurements

K	λ (nm)	E_{exc} (cm^{-1})	A (10^8 s^{-1})
1	307.844	32 475	10.0
2	307.995	32 543	17.0
4	308.328	32 779	33.7
5	308.520	32 948	42.2
6	308.734	33 150	50.6
8	309.239	33 652	67.5
9	309.534	33 952	75.8
10	309.859	34 283	84.1
13	311.022	35 462	100.6
14	311.477	35 915	108.8
15	311.967	36 397	125.2
16	312.493	36 906	133.3
17	313.057	37 444	141.5
18	313.689	38 008	149.6
19	314.301	38 598	157.7

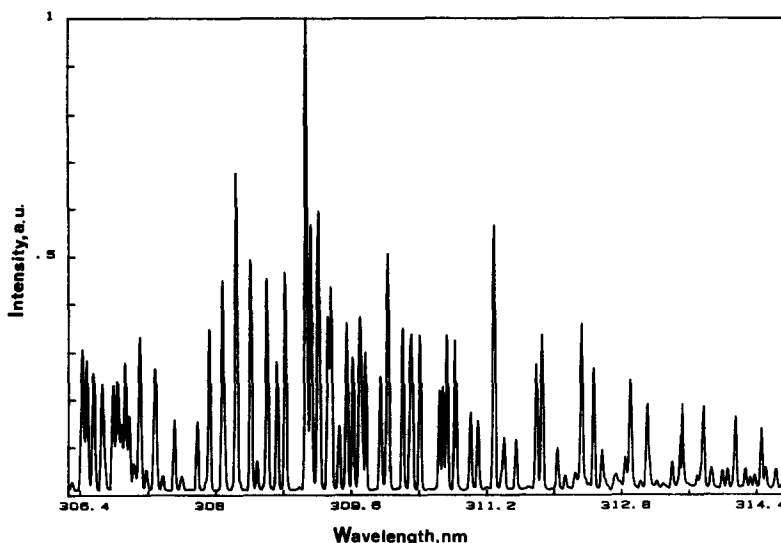


Fig. 8. Spectrum of the (0,0) band of OH emitted by the Ar MIP-surfatron. (Same conditions as Fig. 3.)

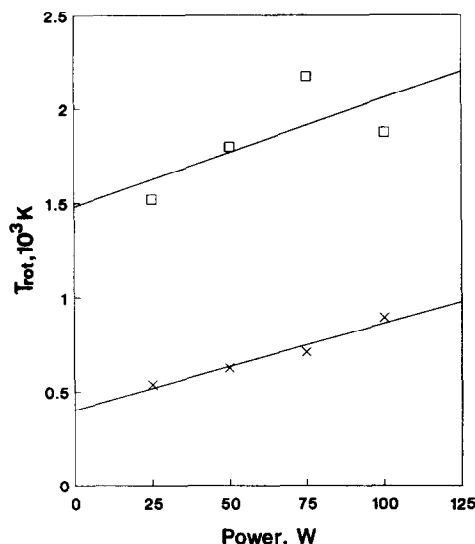


Fig. 9. Rotational temperature vs the net microwave power (\square N_2^+ , \times OH). (Same conditions as Fig. 3.)

electron temperature, T_e (in the 7000–8000 K range) and the heavy particles temperature, T_{rot} (in the 1500–2500 K range); and (b) the obtained electron number density (in the 3×10^{14} – 4×10^{14} cm^{-3} range) is lower than the minimum electron density necessary for the plasma to approach a complete state of LTE taking into account the reabsorption of resonance radiation, i.e. 2×10^{16} cm^{-3} [33–35].

From the experimental results, it is possible to identify different mechanisms by which deviations from LTE conditions can occur. The first is the difference between the electron and heavy particle temperatures. The second probable cause of deviations, is radiative energy loss, which affects the local statistical equilibrium (Boltzmann–Saha) at low electron densities.

To describe the plasma at high pressures (1 atm) and temperatures reaching a few thousand K, the LTE hypothesis has often been used [36]. However, under the combined effects of internal energy losses by radiation escape, energy non-equipartition due to the relative inefficiency of elastic collisions between electrons and heavy particles

of the plasma and transport phenomena, this hypothesis becomes invalid for these partly dissociated and ionized gases. In order to study the population behaviour of the components in these plasmas and then to explain the plasma properties, collisional-radiative models are necessary because the non-equilibrium processes may then be explicitly taken into account. To do this, one must solve a system of equations that couple the populations of the atoms. Numerical solutions of such a system of equations at fixed values of the electron density give the populations of the excited states and, in particular, permit one to pick out the levels that are in relative equilibrium. It is necessary, therefore, in surface-wave-produced plasmas, to elucidate the influence of radiation and collisions on the distributions of excited states and for this purpose, it will be necessary to build up models for the population kinetics of the excited states.

Typical electron number densities in the most conventional ICP device are in the 10^{14} – 10^{16} cm $^{-3}$ range and the electron temperature lies in the 5000–10 000 K range, but the necessary power density is considerably higher than the power density needed with the MIP-surfatron. The latter constitutes, therefore, an attractive device for the purposes of analytical chemistry.

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