MICRO-WAVE DETECTION OF LASER ENHANCED IONIZATION OF METALS IN FLAMES

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Résumé - Dans cet article, la détection à l'aide de micro-ondes des signaux d'ionisation augmentée à l'aide d'un laser est présentée. Le principal avantage de l'utilisation des micro-ondes par rapport à une détection en courant continu est que le champ produit par ces ondes peut être maintenu à si bas niveau que la cinétique de la flamme n'est pas perturbée.

Abstract - In this paper micro-wave detection of laser enhanced ionization signals is reported. The basic advantage of using micro-waves instead of using DC detection is that the micro-wave field can be kept at such low levels that the kinetics of the flame is left undisturbed.

Introduction

In 1976 a group at NBS, Washington, D.C., developed a new laser technique for detection of small traces of atoms and molecules in flames. Instead of using the fluorescence light, that atoms and molecules emit when excited, the ionization enhancement was detected /1/. A DC field was applied to the flame and the laser induced ionization enhancement was measured as a current increase through the flame. This method proved to be very powerful. Densities of metal atoms down to the order of 10^6 atoms/cm^3 have been detected.

However, when studying the flame one has to take into consideration that the presence of a DC field might change the kinetics, since the charges that are created in the flame by thermal processes are extracted from the flame.

In this paper we present a different possibility to detect laser enhanced ionization (LEI) without removing the charges from the flame. This is done by detecting the attenuation of a weak micro-wave field traversing the flame.

Laser enhanced ionization

The process of LEI can be described in the following way:

1. Laser excitation of the trace atom or molecule X:

   $X_{gr} + h\nu \rightarrow X_{exc}$

2. Subsequent collisional ionization:

   $X_{exc} + M \rightarrow X^+ + e^- + M$

   where M is a flame molecule.

Since there exists of the order $e^{\frac{h\nu}{KT}}$ more collision partners with sufficient energy to ionize the excited atoms or molecule, X_{exc}, than collision partners with sufficient energy to ionize the atoms or molecules in the ground state, X_{gr}, the laser excitation leads to a sharp increase of charges in the flame.

This increase of charges is detected in ordinary LEI spectroscopy by applying a DC field across the region of interaction. The laser excitation is followed by a current increase through the flame, which can be easily measured as a voltage increase across a resistor. As mentioned earlier this DC field removes the charges from the flame and might in this way change the kinetics of combustion. There are however alternatives to a DC field for detection of the laser induced charge increase.

Micro-wave absorption

When a micro-wave field is applied to the flame, the charges in the flame are accelerated. The charges will then radiate as dipoles. If a collision disturbs the oscillation, radiation energy is converted into heat. In this way a fraction of the micro-wave field is absorbed.

Belcher and Sugden /2/ showed that the attenuation can be written:

$$\beta = \frac{C\cdot 2\pi e^2 n}{mc_0} \, \frac{\nu}{\omega^2+\nu^2} ,$$

where β is the attenuation in dB/cm, e is the electron charge, n the number of charges per unit volume, m the mass of the charged ion or electron, ν is the collision frequency for the charge and ω is the frequency of the micro-wave field. From this equation it can be seen that electrons will contribute ~100 times more to the attenuation than ions since $\beta \sim \sqrt{\frac{1}{m}}$.

It is also interesting to note that the attenuation decreases when ω is raised above ν. This imposes a upper limit on the micro-wave frequency.

The lower limit for the micro-wave frequency is given by the fact that the spatial resolution is of the same order as the wavelength of the micro-wave field.

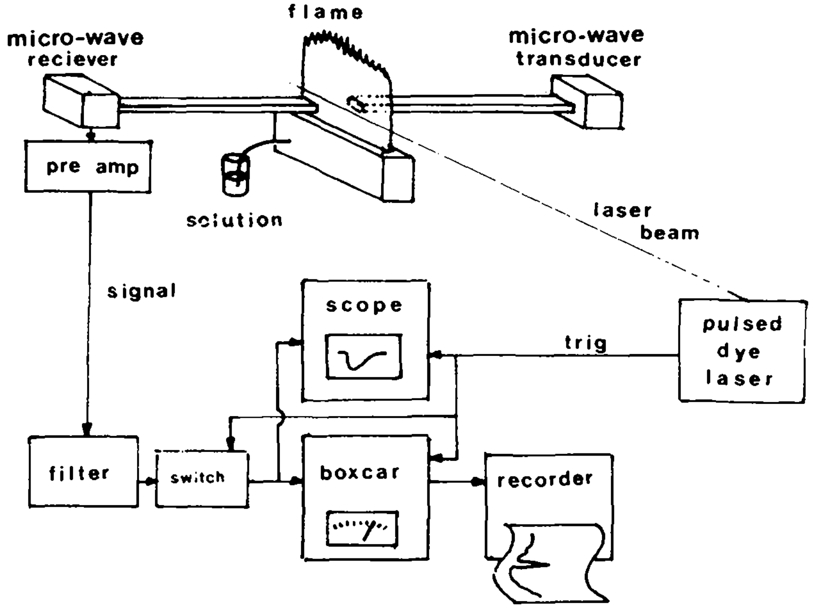

Fig. 1 - The experimental set-up.

Experimental arrangement

The burner used in these experiments was an acetylene/air burner from an ordinary atomic absorption spectrometer. The length of the burner was 10 cm and the width of the interaction region ~1 cm. A water-solution containing sodium was aspired into the burner at a flow rate of ~5 ml/minute.

A pulsed dye laser (Chromatix CMX-4) was used as light source. The pulse energy was ~1 mJ, the pulse duration ~1 µs and the repetition frequency was 25 Hz. The beam diameter was ~3 mm. The beam was directed into the flame ~2 cm above the burner head.

The micro-wave transducer was of Gunn-diode type (Philips PM 7015 X) and gave ~ 10 mW microwave radiation at 10 GHz. A diode (IN23B) was used as receiver. The experimental configuration is shown in figure 1 above.

Results and discussion

The micro-wave absorption signal as a function of time is shown in figure 2.

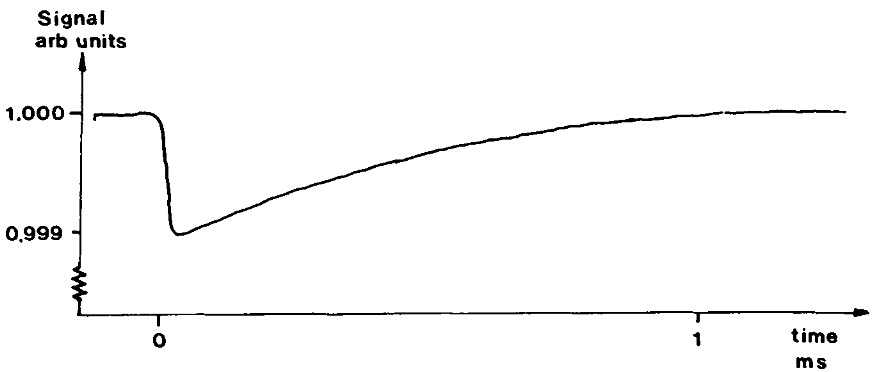

Fig. 2 - Micro-wave absorption signal as a function of time.

In this experiment 10 ppm Na was aspired into the burner and the laser pulse energy was ~2 mJ. This gave rise to $\sim 10^{10}$ electrons/cm^3. The rise time corresponds to the rise time of the laser. The fall time is much longer, probably due to the long recombination time for the electrons.

The created electrons gave rise to an absorption of ~0.1 % of the micro-wave field, in this case ~2.5 µW out of 2.5 mW. This measurement gives us the possibility to estimate the influence on the kinetics due to the micro-wave field.

The 10^{10} electrons absorb 2.5 µW of radiation. Assuming that the kinetic energy the electron absorbs from the micro-wave field is lost when it collides with a molecule in the flame, which happens $\sim 10^{11}$ times per second, the kinetic energy build-up between collisions is $\sim 2.5 \cdot 10^{-6} \cdot 10^{-10} \cdot 10^{-11} \approx 10^{-27}$ J/electron or $\sim 10^{-8}$ eV/electron which is negligible compared to the thermal energy.

It is also possible to give an estimate of the overall heating of the flame due to the micro-wave field. Assume that the flame contains $\sim 10^{10}$ electrons/cm^3. The flame is exposed to the radiation ~0.01 seconds. During this time 0.025 µJ of radiation is converted into heat. This is spread out over ~10^{18} molecules. This gives ~$10^{-8} \cdot 10^{-18}$ J/molecule or 10^{-7} eV/molecule, which is also negligible compared to the thermal energy.

From the considerations above we can conclude that we operated at sufficiently low power of micro-wave radiation that the kinetics of the flame were unchanged.

Figure 3 shows the signal for 10 ppm Na when the laser wavelength was scanned from ~588-590 nm.

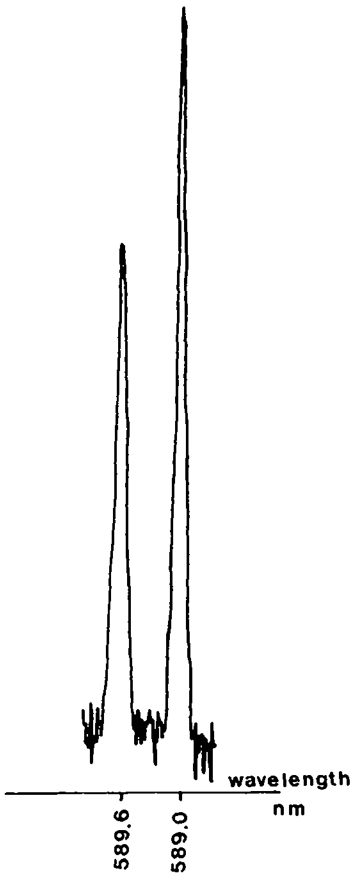

Fig. 3 - Signal vs wavelength for 10 ppm Na

Figure 4 shows the signal for 0.1 ppm Na when the laser was scanned around the $3s_{1/2}$ - $3p_{3/2}$ transition. 0.1 ppm seems to be the detection limit for the system used. This detection limit is ~1000 times higher than the detection limit for ordinary LEI.

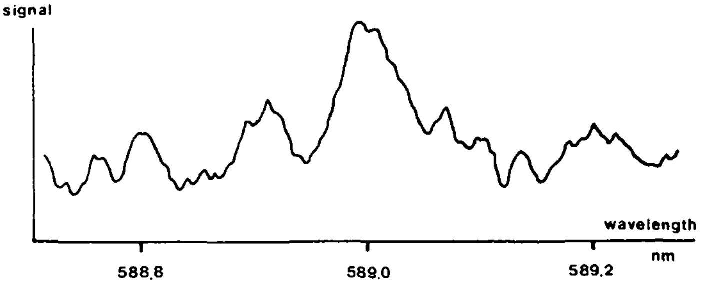

Fig. 4 - Signal vs wavelength for 0.1 ppm Na.

The main contributor to the noise in the system was variations of the micro-wave transducer output. This can be reduced by a more careful choice of transducer and by using an interference technique where the micro-wave field is split in two parts, one passing outside the interaction region and one passing through the interaction region. Figure 5 shows the signal as a function of Na concentration.

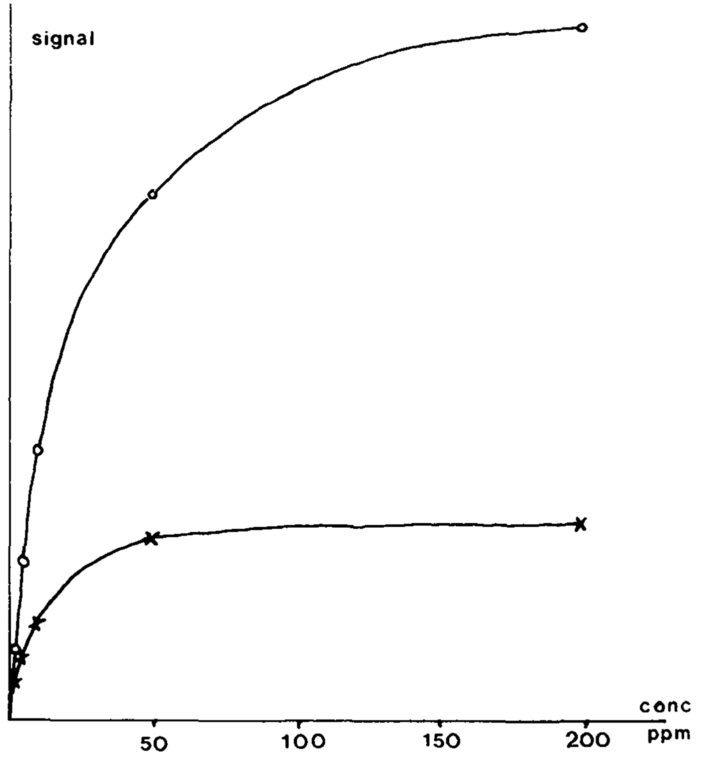

Fig. 5 - Signal vs Na concentration.
Trace A: The waveguides placed where the laser beams enters the flame.
Trace B: The waveguide placed where the laser beam exits the flame.

Figure 5 shows that the upper limit of detection is higher for micro-wave detection than for ordinary LEI where space charge effects tend to destroy the linearity at lower concentrations. For micro-wave detection light absorption seems to give the upper limit of detection.

Conclusions

Micro-wave detection of LEI signals is feasible, though it gives ~1000 times worse detection limits than ordinary LEI. The advantage of micro-wave detection, when used for flame studies, is that the micro-wave field does not change the kinetics of combustion. Another advantage seems to be that the signal is unaffected by space charge effects.

References

1. Green et al., J. of the Am. Chem. Soc., vol. 98, no 26, 1976, p 8517-8518.

2. H. Belcher and T.M. Sugden, Proc. of Royal Soc. of London Sec. A, Vol. 201, 1950.