

Microwave induced plasmas for the analysis of molecular components in incinerator gases

Citation for published version (APA):

Timmermans, E. A. H., Jonkers, J., Mullen, van der, J. J. A. M., & Schram, D. C. (1997). Microwave induced plasmas for the analysis of molecular components in incinerator gases. In P. Fauchais (Ed.), *Progress in Plasma Processing of Materials 1997 : Proceedings presented at the International Thermal Plasma Processes Conference, 4th, Athens, July 15-18, 1996* (pp. 299-306). Begell House Inc..

Document status and date:

Published: 01/01/1997

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Microwave induced plasmas for the analysis of molecular components in incinerator gases

E.A.H. TIMMERMANS, J. JONKERS, J.A.M. VAN DER MULLEN AND D.C. SCHRAM

*Department of Physics, Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven (the Netherlands)*

Abstract — The behavior of molecules in different microwave induced plasmas (MIPs) has been studied by means of optical emission spectroscopy (OES). This in order to study if MIP-OES can be used for the analysis of molecular components in incinerator gases. Various molecular species (i.e. N_2 , CO_2 , SF_6 , H_2O and SO_2) have been introduced into argon or purely molecular plasmas at both atmospheric and reduced pressure. Emission from originally introduced molecules is only observed in the case of nitrogen (emission bands from the first and second positive system). Using other molecular gases, only dissociation and association products are observed (i.e. atomic species, CN , C_2 , CO , OH , NH). The intensity of these products has been studied as a function of the pressure, the concentration of introduced molecules and the position in the plasma. Because mainly association products are observed, is it not straightforward to analyze molecular components in incinerator gases with MIP-OES. Moreover, emission from N_2 , the dominant molecule in incinerator gases, is very intense and extends from 290 to 1000 nm, covering almost this entire spectral range with bands.

1. INTRODUCTION

For years, inductively coupled plasmas (ICPs) [1,2] and microwave induced plasmas (MIPs) [3-5] have been used as excitation sources for the determination of elements. Although ICPs have been used more frequently, MIPs have shown considerable potential as spectrochemical sources in analytical chemistry as well. Advantages of the MIP compared to the ICP are the lower power requirements, the lower gas flow and the larger range of plasma conditions (e.g. pressure, electron

density and temperature). Moreover, microwave generators are readily available (surely at 2.45 GHz) and less expensive than the generators used in ICPs.

Introduction of molecular species has a negative effect on the remaining excitation power for the atomic analyte. Another problem are the strong and broad emission bands of introduced or generated molecules in the plasma. Detection limits are strongly reduced if lines of the analyte interfere with those bands.

Although the effects of these molecules have always been considered as 'unwanted', only few efforts have been made to obtain more information on the precise processes involved in molecular dissociation and recombination [6-8].

The aim of this paper is to provide a better insight into the molecular processes involved in MIPs in order to study the possibility of using MIP-OES for the analysis of incinerator gases. Various plasma applicators (two torches, two surface wave launchers and a resonance cavity) have been used to obtain a widely varying range of plasma conditions (pressure $p \approx 10^{-3}$ -1 bar, electron density $n_e \approx 10^{18}$ - 10^{21} m⁻³, heavy particle temperature $T_h \approx 500$ -4000 K and electron temperature $T_e \approx 4000$ -20000 K). Where possible, different carrier gases have been used: argon, nitrogen and carbon dioxide. In these plasmas varying concentrations of molecular gases (i.e. N₂, CO₂, SF₆, H₂O and SO₂) have been introduced.

2. EXPERIMENTAL AND INSTRUMENTATION

In order to create a wide range of different plasma conditions, five field applicators (all operating at 2.45 GHz) have been used:

- The TIA (from 'torche à injection axiale', using the nomenclature of the developers, MOISAN *et al*) [9-12], creating a free expanding atmospheric flame-like argon or helium plasma. When the nozzle described in [10] is used, pure molecular gases can be used as well.
- The MPT (from "microwave plasma torch", developed by JIN *et al* [3]), creating a free expanding atmospheric flame-like argon plasma in open air.
- The guide-surfatron [13,14], creating an atmospheric capillary argon surface wave discharge.
- The surfatron [13,14], creating a capillary argon, nitrogen or carbon dioxide surface wave discharge at reduced pressure ($p \approx 1$ -10 mbar).
- The Beenakker cavity [4], creating an argon, nitrogen or carbon dioxide plasma at reduced pressure ($p \approx 1$ -20 mbar) enclosed by a quartz tube with an inner radius between 3 and 8 mm.

A rectangular waveguide (WR-340, inner dimensions 86.1 X 42.9 mm) is used for the energy transfer from the magnetron (Philips YJ1442) towards the TIA, the

Beenakker cavity and guide-surfatron. In case of the surfatron and the MPT, a coaxial feed line is used for the energy supply from the microwave generator (Microtron 200 Mark II)

The (simplified) set-up in combination with the TIA is shown in figure 1. The emission signal of the flame-like plasma is guided through an optical fiber and focused on the entrance slit of a 1 meter monochromator (Jobin Yvon Monospec 100, 1200 gr/mm grating, 15 μm entrance slit). A computer-controlled CCD camera (SBIG ST-6, 750 X 242 pixels, each 11.5 X 27 μm in size) is used to acquire the spectra.

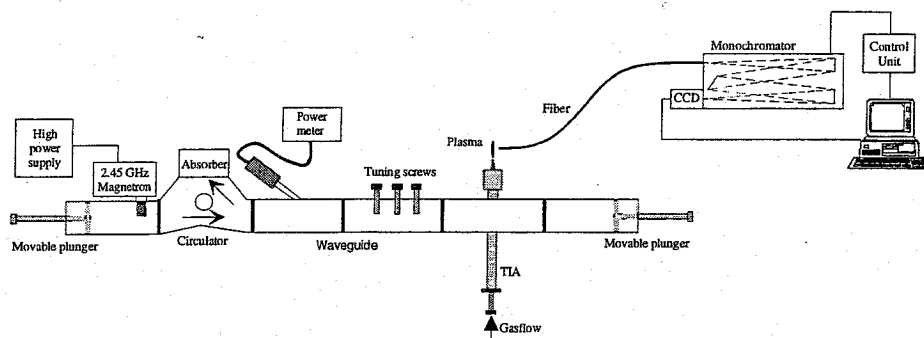


Figure 1. The set-up in which the TIA is used to create an expanding plasma. Through an optical fiber the emission signal of the plasma is guided to a monochromator. Spectra are acquired with a CCD camera.

Table 1 shows some typical operating conditions for the five used field applicators. The given plasma lengths are for pure argon plasmas.

Table 1. Some typical operating conditions

	power input (w)	pressure	carrier gas	max. conc. (%) mol. gases	gas flow (l min^{-1})	appearance	plasma length (cm)
TIA	320	atmospheric	argon, N ₂ , CO ₂	100	4	open air	5
MPT	150	atmospheric	argon	10	1	open air	2
Guide-surfatron	200	atmospheric	argon	5	0.5	quartz tube (0.5 mm)	8
Surfatron	100	1-10 mbar	argon, N ₂ , CO ₂	100	?	quartz tube (3-6 mm)	14
Beenakker	200	1-20 mbar	argon, N ₂ , CO ₂	100	?	quartz tube (3-8 mm)	4

3. RESULTS

3.1. Atmospheric pressure plasmas

The atmospheric pressure plasmas are obtained with the TIA, the MPT and the guide-surfatron. Figure 2 shows a spectrum acquired with the TIA. Note that introduced CO_2 (dissociation energy $E_{\text{dis}}=5.45$ eV) and N_2 ($E_{\text{dis}}=9.76$ eV) can not be observed. In stead, N_2^+ (the first negative system, $\text{B}^2\Sigma^+_u \rightarrow \text{X}^2\Sigma_g$), atomic lines and several association products are seen: CN (the violet system, $\text{B}^2\Sigma \rightarrow \text{A}^2\Pi$), C_2 (the Swan system, $\text{A}^3\Pi_g \rightarrow \text{X}^3\Pi_u$), NH (the 3360 Å system, $\text{A}^3\Pi \rightarrow \text{X}^3\Sigma$) and OH (the 3064 Ångström system, $\text{A}^2\Sigma \rightarrow \text{X}^2\Pi$). Especially the emission of CN is extremely intense (note that the major band heads of CN exceed the range of the graph by far). The strong emission from CN can still be observed if pure CO_2 is used as carrier gas, suggesting a high diffusion rate of the surrounding air into the plasma. The OH radical originates from the dissociation of H_2O , which is always present at trace level as a pollution in argon. Not shown in the spectrum but readily to observe, is the γ system of NO ($\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi$).

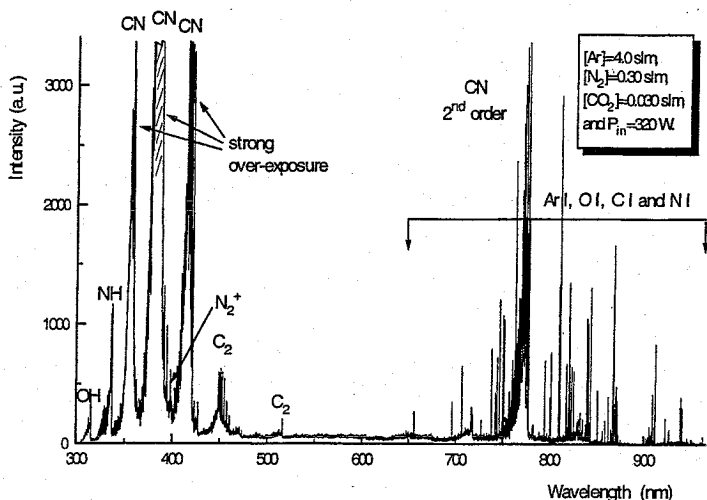


Figure 2. Emission spectrum between 300 and 965 nm of an argon plasma (created with the TIA) in which small amounts of CO_2 and N_2 are introduced. Note the strong influence of associated molecules on the spectrum. The CN band heads of the violet system exceed the intensity range in the spectrum by far. There is no emission from originally introduced molecules.

In figure 3 the intensities of several atomic and molecular species are depicted as a function of the amount of CO_2 injected into a plasma created by the TIA. Note that NI and NH decrease and that the growth of OI is significantly less than the growth of CI or CN. One can observe that the growth of all species is (far) less than

proportional. The excitational power of the plasma hence decreases because of the energy required for dissociative processes.

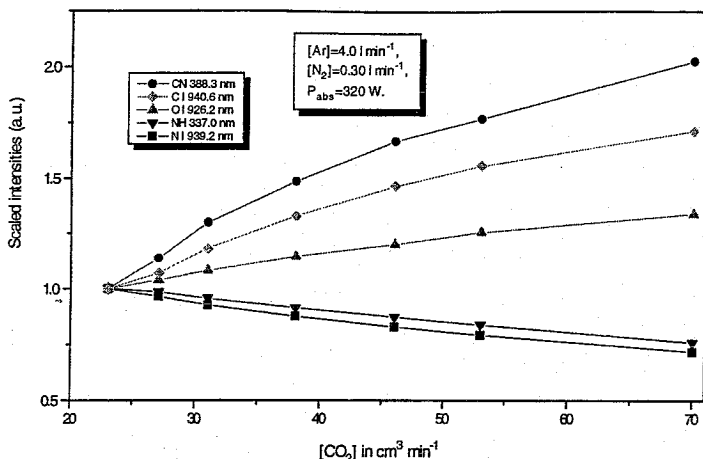


Figure 3. The intensities of several atomic and molecular species as a function of the amount of CO₂ added to the argon/nitrogen mixture. Intensities of CN and C I increase faster than O I while NH and NI decrease (due to decreasing excitational power and association of CN).

When air is used as carrier gas in the TIA, the first and second positive system of nitrogen can be observed, extending from approximately 290 to 1000 nm.

The results with the MPT are similar, although due to the lower maximum power supply (< 200 W), lower concentrations of molecular species can be used. Also for this plasma a strong influence of penetration by surrounding air can be observed.

The introduction of CO₂ into a capillary argon plasma created by the guide-surfatron yields intense C₂ emission while CN is rather weak. Molecular species reduce the length of an argon plasma considerably. Injection of SO₂ (dissociation energy 5.66 eV) results in emission of S I and O I lines. No bands of SO₂ or SO are found, which indicates that SO₂ either does not get excited or is fragmented completely.

Since mainly association products are observed and the intensities of these molecules are non-linear with the concentration, it will be difficult to use atmospheric MIPs for the analysis of incinerator gases. Moreover, atmospheric torches suffer from the disadvantage of penetration by surrounding air. In incinerator gases, the different molecules of interest often contain the same elements and thus will result in the same association and dissociation products in the plasma. Plasmas in which dissociation of molecules is less might give better results.

3.2. Reduced pressure plasmas

At reduced pressure a large discrepancy exists between the electron temperature and the heavy particle temperature (typically 10000 K and 1000 K respectively). The collision frequency of heavy particles mutually is lower and therefore association partly disappears. Instead, dissociation products or original molecules can be observed.

In case argon is used as main gas, a similar behavior as with the atmospheric guide-surfatron plasma can be perceived: the introduction of molecular species (N_2 , CO_2 , SO_2 , SF_6) reduces the plasma length considerably, atomic lines and associated molecules are observed and emission from originally introduced molecules is absent. In figure 4 some intensities are given as a function of the distance to the launching gap of the surfatron. Note that C_2 decreases about twice as fast as O I and Ar I.

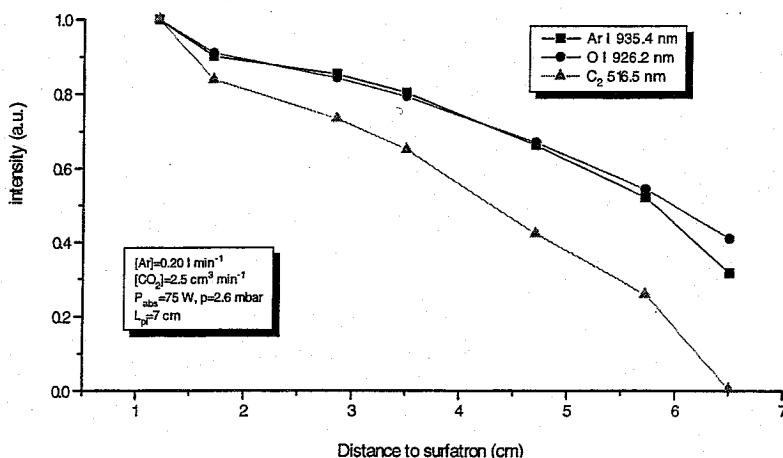


Figure 4. Scaled intensities of an oxygen line, an argon line and a C_2 band head as a function of the axial position in the plasma column. The intensity drop away from the launching gap is significantly larger for the C_2 radical. Experimental settings are given in the plot.

In figure 5 the intensities of C_2 and CN are shown as a function of the amount of N_2 introduced into a surfatron plasma. C_2 shows a constant decrease while CN shows an explosive growth for low nitrogen concentrations, but saturates for higher nitrogen concentrations.

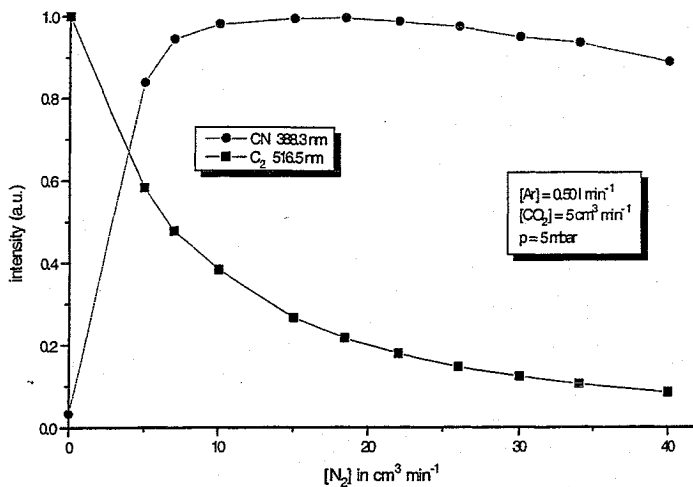


Figure 5. Intensities of CN and C₂ as a function of [N₂] with [Ar] and [CO₂] kept constant. CN reaches its maximum as [CN] ≈ [N₂]. The emission of C₂ however, remains decreasing for higher nitrogen concentrations.

From a discharge in CO₂ at $p < 5$ mbar (created by the surfatron or the Beenakker cavity), emission of the dissociation product CO ($\text{Ångström system, } B^1\Sigma \rightarrow A^1\Pi$) is present while emission of C₂ is absent. With increasing pressure suddenly CO emission disappears and C₂ is observed (turning point $p \approx 5$ mbar). The association of C₂ is not straightforward: at reduced pressure the influence of three-body recombination has to be neglected and no simple two body collision can be found which allows the creation of C₂. Probably the cold quartz tube plays an important role in this process.

From a discharge in nitrogen (at $p < 20$ mbar), the first and second positive system of nitrogen ($B^3\Pi \rightarrow A^3\Sigma$ and $C^3\Pi \rightarrow B^3\Pi$ respectively) can be observed readily.

Although at low pressure dissociation is less, emission from originally introduced molecules is still hardly observed. In general, it can be expected that large molecules (three atomic or more) can not be seen. Moreover, emission from nitrogen (the first and second positive system) is easily observed and covers almost the complete spectral range with molecular bands. Since nitrogen is the major component in incinerator gases, interference of other species with these bands easily occurs.

4. DISCUSSION

Several microwave induced plasmas have been studied with respect to their molecular emission properties. It is found that the plasma surroundings (open air or a quartz tube) and the pressure (atmospheric or reduced) have a large influence.

Spectra from atmospheric pressure plasmas are dominated by association products (e.g. CN, C₂, NH, OH, NO) and atomic species. Only at reduced pressure original species can be seen: introduction of nitrogen results in emission of the first and second positive system of nitrogen. Whereas at higher pressures CO₂ gets dissociated completely, at low pressure fragmentation is only partially since the Ångström system of CO can be observed.

Dissociation and association are major problems for the analysis of molecular components in incinerator gases, hence it is not straightforward to use emission spectroscopy. Another problem consists in the wide and intense emission bands of N₂, easily overgrowing weak other bands. The nitrogen will have to be removed first to enable the analysis of the other molecular components. A solution might be the combination of gas chromatography with a (capillary) plasma: the molecular species are separated in time and dissociated and excited afterwards in the plasma. In this case association products and atoms can provide unambiguous information about original molecules.

REFERENCES

- [1] A.Montaser, *CRC Critical Rev. Anal. Chem.* **18**(1), 45 (1987).
- [2] P.W.J.M.Bouwman, *Inductively Coupled Plasma Emission Spectroscopy, part I & II*, John Wiley & Sons, USA (1984).
- [3] Q.Jin, C.Zhu, M.Borer and G.Hieftje, *Spectrochim. Acta* **46B**, 417-430 (1992).
- [4] C.I.M.Beenakker, *Spectrochim. Acta* **31B**, 173 (1977).
- [5] A.T.Zander and G.M.Hieftje, *Appl. Spectrosc.* **35**, 357 (1981).
- [6] D.Truitt and J.W.Robinson, *Anal. Chim. Acta* **51**, 61 (1970).
- [7] P.S.Moussounda and P.Ranson, *Spectrochim. Acta* **40B**, 641 (1985).
- [8] E.A.H.Timmermans, J.Jonkers, J.A.M.van der Mullen, A.Rodero, M.C.Quintero, A.Sola and A.Gamero, *To be submitted to Spectrochim. Acta B* (1997).
- [9] M.Moisan, G.Sauvé, Z.Zakrewski and J.Hubert, *Plasma Sources, Science and Technology* **3**, 584 (1994).
- [10] A.Ricard, L.St-Onge, H.Malvos, A.Gicquel, J.Hubert and M.Moisan, *J. Phys. III France* **5**, 1269 (1995).
- [11] J.Jonkers, L.J.M. Selen, J.A.M.van der Mullen, E.A.H.Timmermans and D.C. Schram, "Characterisation of plasmas produced by the 'torche à injection axiale'", *This conference, TPP-4 Athens* (1996).
- [12] J.Jonkers, J.M.de Regt, J.A.M.van der Mullen, H.P.C.Vos, F.P.J.de Groote and E.A.H.Timmermans, *Spectrochim. Acta* **51B**, 1385-1392 (1996).
- [13] M.Moisan and Z.Zakrzewski, *J. Phys. D: Appl. Phys.* **24**, 1025-1048 (1991).
- [14] M.Moisan and J.Pelletier, *Microwave Excitation Plasmas (Chap.V)*. Elsevier Science Publish. B.V., Amsterdam, The Netherlands (1992).