

Microwave induced plasma torches for on-line combustion gas analysis

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Introduction

For many years various different plasmas have been used as excitation sources for the determination of elements using atomic emission spectroscopy (AES).^{1,2} Nowadays, AES is widely used in analytical laboratories, particularly for the analysis of aqueous samples. However, for the analysis of gaseous samples, AES is used less frequently. One of the reasons is the lack of calibration samples for quantitative measurements. Our aim was to study the feasibility of AES for the on-line monitoring of combustion gases of an industrial chemical waste incinerator. As the requirements for the excitation source are substantially different than those for the analysis of aqueous samples, we evaluated several plasma sources for this purpose. The plasma source with the best characteristics was then tested at the waste incinerator site.

The Inductively Coupled Argon Plasma (ICP) is by far the most used plasma source for the analysis of aqueous samples; detection limits achieved by ICP-AES are usually in the sub-ppb range. Microwave induced plasmas (MIPs) are also frequently used in analytical chemistry. In addition to the well-known surfatron³ and the Beenakker cavity⁴ a variety of other field shaping applicators are used.^{5,6} However, major restrictions of most types of MIPs are their sensitivity to water introduction and their limited evaporation and excitation power of analytes. Therefore detection limits of elements are usually worse than for ICP-AES.¹

In this study, we wanted to monitor combustion gases directly above the

combustion process, where hazardous elements are still present in high concentrations. This implies that low detection limits are less essential, whereas insensitivity to molecular gases and a compact hardware are more important. As discussed by Timmermans *et al.*,⁷ the argon ICP has major limitations when the analyte is carried by molecular gases (as is the case for combustion gas analysis). The excitation power of the plasma diminishes when small amounts of molecular gases are injected. Although air or nitrogen ICPs exist, their power requirements are so high (typically > 3 kW), that the experimental set-up would become too large for installation at a waste incinerator.

As an alternative, microwave induced plasmas produced by the TIA (from "Torche à Injection Axiale")^{8,9} and the MPT (from "Microwave Plasma Torch")¹⁰⁻¹² were evaluated and their analytical performances compared. Both torches create atmospheric plasmas that expand into open air, similar to the ICP, and benefit from a compact set-up and low gas consumption (typically 1 to 5 slm). Plasmas have a relatively high electron density and temperature and seem to have overcome the large sensitivity to water vapour, being characteristic for many other MIPs.

Spectroscopic analysis of combustion gases

During the last decade, worldwide several groups have been studying the feasibility of using AES for on-line flue

gases analysis. These studies focused on off-stream exhaust gases, i.e. relatively clean and cold gases just before their ejection into the atmosphere takes place. The main reason for these investigations is the expectation that legislation will soon enforce continuous emission monitoring of flue gases for several industries, e.g. power plants, cement industries and waste incinerators.¹³ Significant progress has been made with ICP-AES.¹³⁻¹⁸ In contrast to the studies of these groups, our aim was to develop analytical equipment that can be used to control the combustion process. This requires compatibility with changing experimental conditions and the presence of acids and dust particles.⁷ As commercially available ICP-AES equipment is developed for relatively clean gases and should be used under laboratory-like conditions, it is not straightforward to use them for our application.

A project was started in co-operation with AVR-Chemie, a large industrial hazardous waste incinerator in Rozenburg (close to Rotterdam), with the aim of on-line monitoring of heavy metals in combustion gases just above the flames of the incineration process itself, i.e. in gases that have not yet been cleaned. Measurements needed to be performed on gases extracted from the so-called secondary combustion chamber that has the function of incinerating hazardous waste that has not been completely burnt inside the rotary kiln.⁷ On-line monitoring could possibly then be used for adjusting the incineration composition, in order to optimise the combustion process or to minimise peak loads of metal flows. This may increase the lifespan of the equipment used for the extensive cleaning steps that follow after the two-stage incineration and thus decrease the downtime of the incinerator plant.

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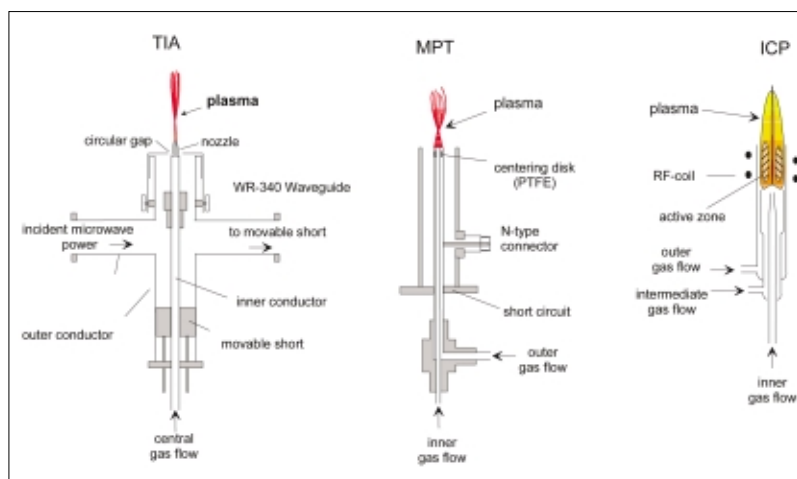


Figure 1. From left to right: the TIA, the MPT and the ICP. Typical plasma parameters and operational settings are given in Table 1.

The TIA and the MPT compared to the ICP

Prior to the measurements at AVR-Chemie, a suitable excitation source needed to be found. As discussed in the Introduction, we focused on the TIA and the MPT. The TIA, depicted in Figure 1 on the left, is a high power microwave-fed plasma torch that can produce atmospheric discharges in various gases. In their first paper about the TIA, Moisan *et al.* already showed that this torch is relatively insensitive to plasma impedance changes.⁸ In combination with the relatively high electron density, electron temperature and heavy particle temperature (see Table 1) this makes it a promising excitation source for spectrochemical analysis. The torch consists of a coaxial structure perpendicular to a rectangular waveguide (WR-340), see Figure 1. Basically, the TIA converts the propagation mode of the incident microwave radiation from the TE_{01} mode inside the rectangular waveguide into the coaxial TEM mode. The plasma carrier gases and aerosols are introduced through the central gas inlet at the bottom of the coaxial inner conductor and expand through the nozzle, which is the top end of the inner conductor. Due to the field shaping characteristics of the TIA, the microwave energy is dissipated on top of the nozzle, where the plasma is created. A more thorough description of the hardware can be found in Timmermans *et al.*¹⁹ A cross-flow nebuliser has been used for the creation of aerosols.^{1,2}

The MPT, depicted in the middle of Figure 1, produces flame-like plasmas.¹¹ The main differences of the MPT com-

pared with the TIA are lower power and gas consumption and its separate central gas channel through which analytes can be introduced. Power is supplied through a coaxial feed line.

The ICP, also shown in Figure 1, is much more voluminous than the TIA and MPT microwave induced plasmas.

Typical plasma parameters and operational settings for the three plasma sources are given in Table 1.^{19–22} Key parameters for optimal aerosol evaporation and analyte excitation are the plasma dimensions, the gas flow configuration, the analyte residence time and the parameters n_e , T_e and T_h . A plasma zone with a high heavy particle temperature, T_h , ensures effective evaporation of the aerosol and dissociation of molecules, whereas a high electron temperature, T_e , (and density, n_e) is desired for the excitation of analytes with high excitation energies. The values listed are typical for argon discharges and may be considerably different when aerosols or molecular gases are introduced.

Laboratory studies

Aerosol injection

Emission spectra were obtained with a Monospec 18 monochromator (15.6 cm focal length, 10 μm entrance slit, 2400 gr mm^{-1} grating, produced by Thermo Jarell Ash) and a UV-enhanced ST6-UV CCD camera (used as a 1D array of 750 pixels, each 11.5 μm wide \times 6.53 mm length, produced by Santa Barbara Instrument Group). The obtained resolution was 0.012 nm pixel⁻¹ at 210 nm. The plasma was imaged onto the entrance slit of the monochromator with a parabolic mirror.

Table 1. Comparison of typical plasma parameters and operational settings of the TIA, MPT and ICP.

Parameter	TIA	MPT	ICP
Electron density n_e (m^{-3})	3×10^{21}	3×10^{20}	2×10^{21}
Electron temperature T_e (K)	20×10^3	18×10^3	12×10^3
Heavy particle temperature T_h (K)	1×10^3 – 4×10^3	1×10^3 – 3×10^3	5×10^3 – 7×10^3
Ionisation degree (%)	1	0.1	2
Applied power P (W)	300–2000	50–300	600–1800
Plasma dimensions (cm^2)	$\varnothing 0.1 \times 5$	$\varnothing 0.2 \times 4$	$\varnothing 2 \times 5$
Typical n_e gradient length (mm)	~ 0.07	~ 0.07	~ 1
Typical T_e gradient length (mm)	~ 0.1	~ 0.1	~ 2
Used frequency f	2.46 GHz	2.46 GHz	10–100 MHz
Suitable carrier gases	Ar, He, N_2 , air	Ar, He	Ar
Gas flows (inner/interm./outer) (slm)	(3–6)/—/—	(0.2–0.4)/(0.3–0.5)/—	1/(0–1)/(10–20)
Skin depth δ (mm)	~ 0.1	~ 0.1	~ 2

First, we compared the emission profile from argon plasmas produced by the TIA and MPT into which aerosols were injected. Typical results are depicted in Figure 2; they show the normalised line-of-sight intensities of a Mg line at different axial heights above the nozzle (AN). Analyte emission from the TIA extends over a broad range along the plasma axis, starting just above the nozzle. Experiments with different analytes (Zn, Mg, Na, Cd) showed that detection limits for the TIA are around 1 ppm for these elements if the aerosol is injected directly into the plasma without any preliminary desolvation process. The distribution of analyte emission is rather different for the MPT, where just above nozzle hardly any analyte signal is present and a distinct emission maximum is found at a height of 8 mm, see Figure 2. Similar plots were observed for other analytes.

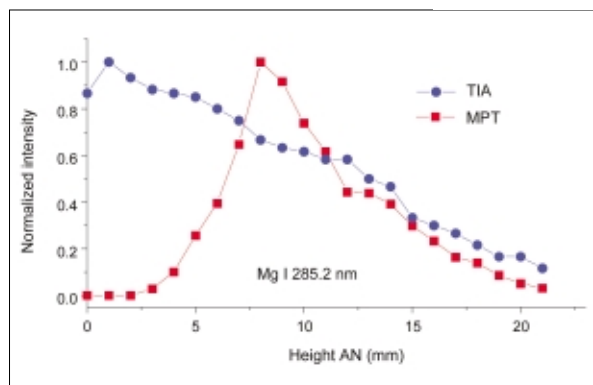


Figure 2. Normalised intensities of a Mg 3p→3s atomic line (at 285.2 nm) from argon plasmas with magnesium analyte injection produced by the TIA and the MPT measured at different heights above the nozzle (AN).

The differences between TIA and MPT can be largely ascribed to the different analyte injection methods: in the TIA aerosols and argon are mixed before being injected into the plasma, whereas in the MPT the analyte is introduced through the central channel along the axis of the (hollow) plasma cone so that the actual plasma penetration of the aerosol takes place in the central zone. Detection limits for the MPT have been reported by Jin *et al.*¹⁰ and are around 0.1 ppm when no desolvation is used.

Influence of molecular gases

Up to now we have only considered aqueous analyte injection. However,

for this application of combustion gas analysis, we have to take into account that the analyte is carried by molecular gases. It is found that, like the argon ICP, the argon MPT is very sensitive to molecular gas injection. Typically only a few percent of molecular gases can be injected into the discharge before the plasma is extinguished. This imposes a major limitation on using the MPT as an excitation source of combustion gases.

The TIA, however, can handle a much larger load of molecular gases, both in an absolute and in a relative sense.²⁰ Depending on the geometry of the plasma, plasmas can even be sustained using solely molecular gases.

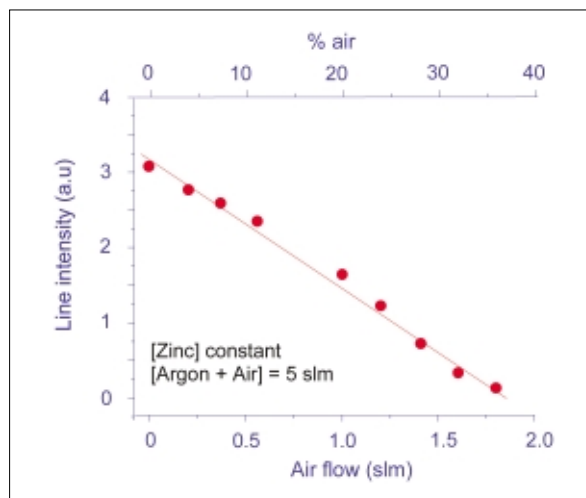


Figure 3. Intensities of a Zn 4p→4s atomic line (at 213.9 nm) as a function of the amount of air added to the argon TIA discharge with aerosol injection. The amount of injected aqueous aerosol is kept constant. Measurements are performed at 10 mm AN, $P = 1$ kW.

In Figure 3, the intensity of a Zn emission line is given as a function of the amount of air additionally added to the plasma. As can be seen from the figure, the analyte intensity decreases fairly smoothly. It should be noted that in the case of combustion gas analysis, the analyte intensity will (at least to some extent) increase with increasing gas flow, as the amount of analyte is proportional to the amount of combustion gases. This is in contrast to the example given, where the amount of Zn analyte is kept constant.

Therefore, despite the poorer detection limits for discharges with aerosol injection only, the TIA is preferred for applications involving molecular gases, e.g. combustion gases.

Experimental data obtained at a waste incinerator

Gas extraction

The pressure inside the secondary combustion chamber at AVR-Chemie is slightly below atmospheric, typically fluctuating between values of 0 to 3 mbar less. As a consequence, combustion gas samples needed to be actively extracted from the incinerator. This was achieved by operating the plasma at a slight under-pressure (typically between 950 and 990 mbar). This is accomplished with the use of a cylindrical vessel that is mounted on top of the waveguide section of the TIA and can be

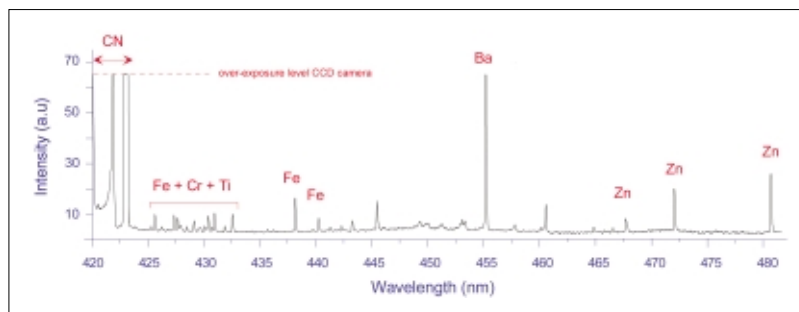


Figure 4. A part of a typical spectrum as measured from a discharge without argon addition. $P = 600$ W, measured at 10 mm AN.

evacuated by a vacuum pump.⁷ The inner conductor of the TIA, being the gas inlet of the torch, is connected to an Al_2O_3 tube that is inserted through an aperture in the incinerator wall. Al_2O_3 was used, as this is one of the few ceramics that is compatible with gases of 1200°C, as present inside the secondary combustion chamber. Due to the pressure gradient between the plasma vessel and the incinerator (with the pressure inside the incinerator being closer to atmospheric), combustion gases will be extracted from the oven and injected into the plasma without the need for a pump between the oven and the plasma.⁷ The stainless steel sampling line between the Al_2O_3 tube inside the incinerator wall and the central pipe of the TIA plasma is typically a few metres long and heated to approximately 150°C in order to minimise transport losses of particulates. The combustion gases can be diluted with argon, just before entering the TIA. By varying the pump capacity the gas flow can be

adjusted. The vessel contains a quartz-viewing window to enable spectroscopic measurements.

General results and discussion

Several elements could be identified from the measured spectra:

Al (394.40, 396.15),
 Ba (455.40, 493.41),
 C (193.09, 247.86),
 Ca (393.37, 396.85),
 Cr (425.44, 427.48),
 Cu (324.75, 327.40),
 Fe (371.99, 438.36),
 Mg (285.21, 517.27),
 Mn (403.08, 403.31),
 Na (589.00, 589.59),
 Pb (368.35, 405.78),
 Si (250.69, 251.61),
 Ti (399.86, 453.32),
 W (272.44, 407.44),
 Zn (202.55, 213.86).

The corresponding strongest emission lines are given (in nm) in brackets.

As an example, a part of a typical spectrum is given in Figure 4. Several

atomic lines can be distinguished in the depicted spectral range between 420 and 480 nm.

In the measured spectra several molecular bands are dominant, especially when the plasma is operated on combustion gases solely: N_2 ($B^3P \rightarrow A^3\Sigma$, $C^3\Pi \rightarrow B^3\Pi$), N_2^+ ($B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$), CN ($B^2\Sigma \rightarrow A^2\Pi$), NH ($A^3\Pi \rightarrow X^3\Sigma$), NO ($A^2\Sigma^+ \rightarrow X^2\Pi$) and OH ($A^2\Sigma \rightarrow X^2\Pi$). In particular the CN emission covers large parts of the spectrum. The molecular background can be reduced by the addition of a considerable amount of argon. Experimentally it is found that the best results are obtained if approximately 2 slm of combustion gases and 3 slm of argon are used to sustain the plasma.

Despite the extreme measurement conditions and the aggressive medium that had to be analysed, the analysis system operated stably for several weeks in which it was used up to eight hours per day. Although not all elements could be measured that would be of interest for process control (e.g. As and Hg are missing), the stability of the system and the number of detected elements listed above, confirm that the TIA is an excellent plasma source for the excitation of combustion gases.

The current diagnostics can only be used to monitor relative fluctuations in the gas composition in time. Obviously, quantitative measurements are desirable. Assuming that losses of particulates, containing a large fraction of the relevant elements, are avoided with the use of the heated sampling line, it will still be difficult to calibrate the system. This is mainly because gaseous standards containing all relevant elements are not yet available. Thorough knowledge of changes in plasma properties when molecular gases are injected may eventually lead to quantitative measurements without the need of a calibration standard.

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