

# Real time analysis of metallic pollutant (CuO) by inductively coupled plasma system without calibration stage

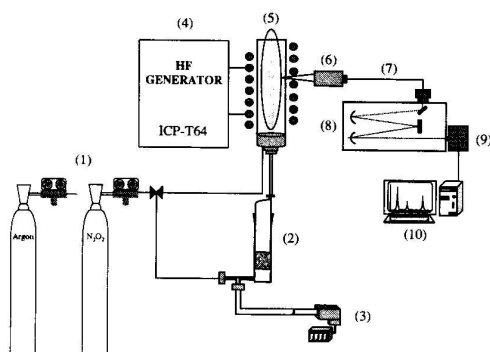
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A method contributing to real-time analysis of metallic pollutant present in stack gas is investigated. This method is based on spectroanalysis using an ICP torch system without any calibration step. The fluidized bed technology is used to simulate heavy metal emission. The massic fluxes of copper oxide (CuO) are determined by using the intensities ratios of the metallic element spectral lines with those of the plasma gas element (argon or dry air). These ratios and the plasma characteristics (atomic excitation temperature  $T_{exc}$ , degree of thermal disequilibrium  $\theta$ ) are inserted into a calculation code of plasma composition to determine the massic flux. A study of the fluidized bed properties is made to correlate the values with those resulting from the elutriation calculation of the copper oxide.

## 1. Introduction

The industrial atmospheric emissions, as a result of combustion or incineration processes, tend to be periodically controlled, especially for the heavy metals. The ICP technology shows the best sensitivity for the detection of these species [1]; however, the main problem still is the calibration stage. A method for continuous metals emission monitoring by ICP system without calibration is proposed. The fluidized bed technology is used to inject directly the pollutants (CuO) into the ICP torch (Figure 1).



**Figure 1.:** Schematic representation of the experimental set-up. 1 - plasma gas, 2 - fluidized bed, 3 - pressure captor, 4 - HF generator, 5 - plasma (dry air or argon), 6 - optical probe, 7 - optical fibre, 8 - spectrometer, 9 - detector : CCD matrix, 10 - computer.

The plasma torch can operate using either argon or air as plasma gas (Table 1). For this two kinds of plasmas, different quantities of a metallic pollutant

(CuO) are introduced in a fluidised bed composed mainly of silica sand and injected in the plasma. The intensities ratios Cu510 nm / ArI518 nm and CuI 793 nm / OI777.19 nm are registered for each CuO proportion (Table 2) and inserted, after the Abel inversion application, into the plasma composition calculation code. This code uses the Gibbs free energy minimization [2]. The aim of the operation consists to adjust by dichotomy the experimental intensities ratios with the theoretical ones in order to determine the initial proportion of the pollutant element in the plasma. The final value resulting from the composition calculation code gives the molar percentage of copper in the plasma, which is converted in massic flux ( $\text{kg}\cdot\text{s}^{-1}$ ) by intermediates calculations.

		argon	dry air
<b>HF generator</b>	power (kW)	2,53	2,53
	inductor coils	5	7
<b>Flow rate (<math>\text{l}\cdot\text{min}^{-1}</math>)</b>	plasma	24	20
	fluidisant	0,54	0,54
	pressure	atmospheric	atmospheric
<b>Optical set-up</b>	gratings	1200	1200
	acquisition time (s)	10	10

**Table 1:** Main features of the experimental equipment.

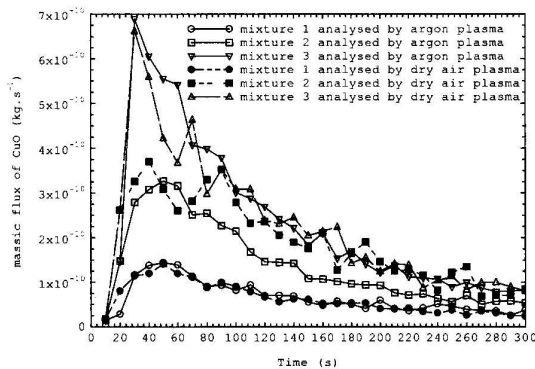
	Silica sand (g)	Copper oxide (mg)
Mixture 1	10,0	2,6
Mixture 2	10,0	5,2
Mixture 3	10,0	10,1

**Table 2 :** Composition of the fluidised bed.

The experimental results are then compared with those resulting from the elutriation constant calculation (Baeyens and al. formula [3]). The following hypotheses have been made : the particles of CuO are spherical, have a mean diameter equals to 4  $\mu\text{m}$  and 40% of the initial mass of copper oxide introduced in the fluidised bed are potentially elutriable.

## 2. Results

Figure 2 reports the temporal evolution of the massic flux of copper oxide for the three different mixtures of silica sand and CuO (Table 2). The results obtained for the two kinds of plasmas are placed on the same graph in order to compare the values. For each CuO proportion in the silica sand bed, the massic fluxes are relatively equals whatever argon or dry air plasma are used. Moreover, the analytic system response is linear.



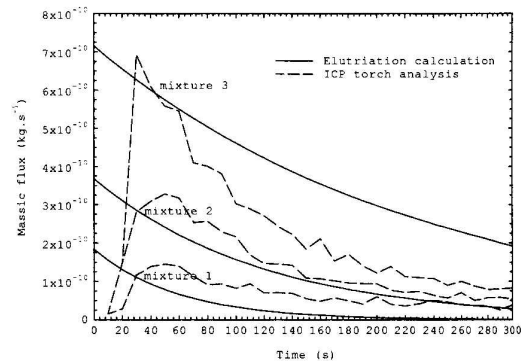
**Figure 2.:** Evolution of the massic flux of copper oxide particles as a function of time, mass initially introduced in the fluidized bed and kind of analysis plasma.

Figure 3 reports the massic fluxes obtained with the elutriation constant calculation for each mixture in comparison with the massic fluxes obtained experimentally. The agreement between the curves is fairly good.

The parameters which can modify the results are the following : the atomic excitation temperature and the thermal disequilibrium values. The influence of each parameter has been studied :

- the experimental determination of the atomic excitation temperature implies an uncertainty close to 200 K that is caused by the transition probabilities accuracy. A 200 K variation multiplies or divides the massic flux by a factor 3/2 and 2 respectively for the argon and the dry air plasma;

- concerning the dry air plasma, where a little departure from equilibrium is present ( $\theta = 1,1$ ) [4], a variation of 0,1 of  $\theta$  modifies the results by a factor between 1,2 and 1,4.



**Figure 3.** Comparison of the massic fluxes obtained by the two calculation methods. Argon is the fluidisant gas.

## 3. Conclusion

The real time detection method, based on the direct analysis of the spectral lines intensities ratios between the pollutant and the plasma gas element, without the usually calibration process is quite promising. The study should be extended to every metallic pollutant present in industrials emissions (Pb, Cr, As, Zn, Cd, Mn,...). Then, it will be necessary to connect the ICP system to a combustion or incineration oven in order to apply our detection process in real conditions of pollutants emissions.

## 4. References

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