

Determination of size distribution and chemical composition of fine particulate emissions from cement kilns

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## **SUMMARY**

Although the monitoring of fine particulate from industrial emissions is becoming of growing interest, fine particulate emissions from cement kilns are poorly characterised. This paper presents a study of characterisation of the size distribution and the chemical composition of fine particles emissions from cement kilns. It was financially supported by the French technical association of the cement industry ATILH and the French environment agency ADEME and was carried out by INERIS in collaboration USTL-CNRS.

This work follows a first program (GAEC, 2005; GAEC, 2007) which aimed at evaluating different measurement techniques for the characterisation of fine particles stack emissions. One of the objectives of the project was to focus on the determination of PM concentrations using cascade impactors sampling. This technique that was selected by the ISO working group dealing with the topic of PM<sub>10</sub> and PM<sub>2.5</sub> measurements from stack emissions below 40 mg/m<sup>3</sup><sub>0</sub> (ISO TC 146 SC1 WG 20), showed very good operational and metrological characteristics (Fraboulet et al, 2007).

The aim of the present study was firstly to evaluate the capabilities of the association of cascade impactors sampling together with chemical and single particle analysis to characterise PM stack emissions from cement kilns, and to improve the state of knowledge of the French cement industry on its fine particulate emissions.

Four sampling campaigns were performed on four cement kilns equipped with different production processes (dry and semi-dry) and different dust abatement processes (ESP dust filter or bag filters). The parameters of interest were PM mass fractions (PM<sub>10</sub>, PM<sub>2.5</sub>, PM<sub>1</sub>), and chemical species selected because they are major components of the aerosol or because of their potential impact on human health.

This paper gives feedback on the sampling and analytical strategies, recommendations of best practices for the determination of low emissions (below 20 mg/m<sup>3</sup><sub>0</sub>), and shows some characterisation results.

## **INTRODUCTION**

Emissions of particulate matter with an aerodynamic diameter smaller than 10 µm (PM<sub>10</sub>) have become of growing interest. Since 2003, a standardisation working group dealing with PM<sub>10</sub> and PM<sub>2.5</sub> emissions from stationary sources has been set up (ISO TC 146 SC1 WG 20); a standard based on the use of manual cascade impactors sampling for the determination of PM<sub>10</sub> and PM<sub>2.5</sub> mass concentrations below 40 mg/m<sup>3</sup><sub>0</sub> is being prepared and is about to be published.

Through various sampling campaigns carried out on industrial stacks, INERIS acquired good knowledge in using this technique as well as feedback concerning its capabilities and limits. The use of manual cascade impactors together with in lab analyses appeared as a promising application that needed to be evaluated. The program presented here was financially supported by ATILH and ADEME and aimed at testing the capabilities of such a combination and improving the state of knowledge on the characterisation of the size distribution and the chemical composition of fine particles emissions from cement kilns.

A first step consisted of a state of the art of the available measurement techniques and results of characterisation of cement plant emissions. Sampling campaigns were performed on four cement kilns equipped with different production processes (dry and semi-dry) and different dust abatement processes (ESP dust filter or bag filters) using three-stage manual cascade impactors equipped with PTFE (Teflon) or quartz filters.

The study focused on:

- the aerosol size distribution, the parameters concerned were TSP (Abdul-Wahab 2006), PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> mass concentrations
- the chemical characterization of the PM fractions. Characterization of chemical species was performed by chemical and single particle analysis.

Two classes of chemical species have been considered:

- species that are the main contributors of the aerosol mass such as ions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) organic (OC) and elemental carbon (EC), some metals (Ca, Si, Al, Mg, P, Fe)
- species that have a potential health impact such as 15 PAHs, trace metals (Journal officiel du 10 octobre 1996; Journal officiel du 20 septembre 2002)

## **MATERIAL AND METHODS**

### **Measurement sites**

<b>Plant</b>	<b>Production process</b>	<b>Treatment process</b>	<b>% of waste burnt</b>	<b>Expected TSP concentration [mg/m<sup>3</sup>]</b>
A	Dry	ESP dust filter Denox SNCR	33	10
B	Semi Dry	Bag filters Denox SNCR	36.7	1
C	Dry	Bag filters	36.9	<5
D	Semi Dry	ESP dust filter Denox SNCR	61	6

### **Measurement methods**

#### **Sampling:**

For both methods, isokinetic sampling was performed, on site blank filters were prepared in order to prevent any risk of contamination during storage, transport and set up of the sampling lines.

- TSP samplings were carried out according to NF EN 13284-1 reference gravimetric method.
- PM gravimetric fractions were performed using a DEKATI cascade impactor according to the PR NF EN 23210. Sampling time must be adapted to expected concentrations and depends on the type of analysis to be carried out afterwards. For gravimetric determination, a compromise should be found between collecting enough matter and avoiding the saturation of impaction plates. For trace analysis the amount of dust collected should be maximised whereas for single particle analysis, agglomeration of particles should be avoided.

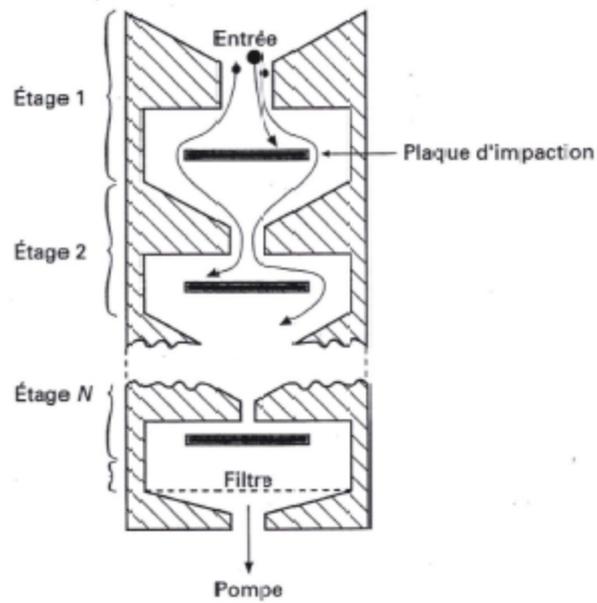


Figure 1 : principe of a manual cascade impactor

**Analytical methods:**

➤ **Gravimetric determination**

PM gravimetric determinations were carried out in a controlled humidity (50%), temperature (20°C) weighing room. Weighing operations were done using Metler Toledo MT5 balance with a resolution of 1µg.

TSP gravimetric determinations were performed according NF EN 13284-1 standard. In both cases, 3 blank filters were weighed with each batch of sampling filters before and after sampling and transported on site. The average difference between weighing operations of these blank filters were subtracted from the sampling masses.

➤ **Chemical characterization**

Chemical analyses for the quantification of chemical species

Target species	Sampling Filter material	Filter conditioning	Analytical method
Metals	PTFE	none	Sample digestion with HF/HNO <sub>3</sub> mixture according to <b>NF EN 14385</b> Analyses by ICP-OES analysis according to <b>NF EN ISO 11885 1998.</b>
16 Trace metals	quartz	none	Sample digestion with HF/HNO <sub>3</sub> mixture according to <b>NF EN 14385</b> Analyses by ICP/MS according to <b>NF EN ISO 17294-2</b>
Chromium VI speciation (soluble and non-soluble )	quartz	non	Analysis according to <b>Metropol 84</b> Metropol 2005) french standard
15 PAHs	quartz	450°C-12h	Ultra sons acetonitrile extraction according to <b>NF X 43-025</b> analysis by HPLC/UVHPLC/Fluorimeter
Ions (Anions-Cations)	PTFE	none	Extraction by a water(95%)-isopropanol (5%) solution  Analysis according to <b>EN ISO 14911</b> for cations and <b>EN ISO 10304</b> for anions
Organic carbon (OC) and elemental carbon (EC)	quartz	none	Analysis according to <b>NF 14530.</b> Infra red absorption analysis of the CO <sub>2</sub> emitted during a pyrolysis phase at 500°C under N <sub>2</sub> atmosphere (OC) followed by 750°C under O <sub>2</sub> atmosphere (EC)

Single particle analysis..

MEBE (Environmental Electronic microscope) coupled with an Energy Dispersive Spectrometer (EDS) was used at INERIS on sampling filters collected at site A for the validation of the size distribution of the dust collected onto the impactor filters.

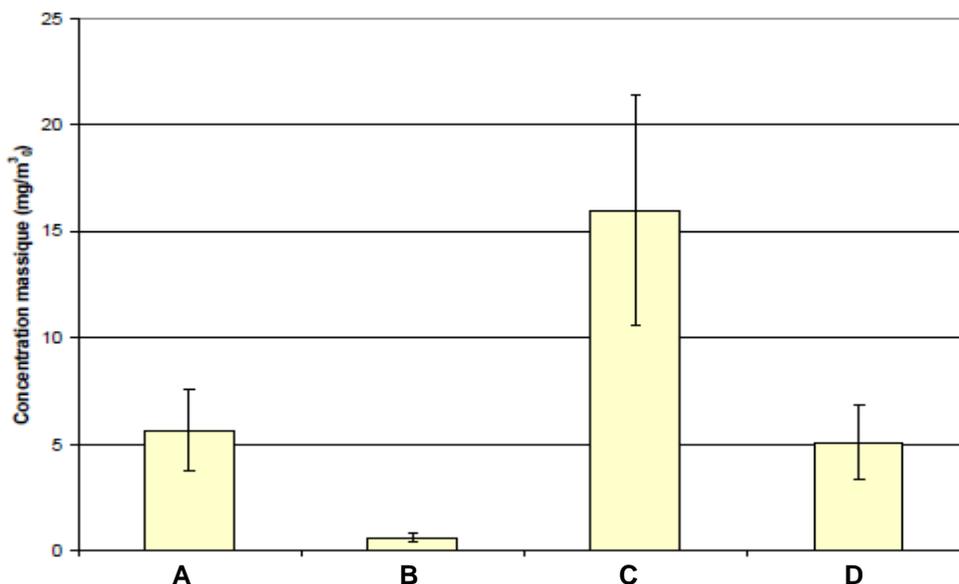
The combined used of MEBE-EDS and Raman microspectrometry was used at USTL-CNRS and provided elemental composition and molecular mapping within single particles according to a previous study (Batonneau et al., 2006)

These single particle analysis techniques were preferentially performed on PTFE filters and requires very small amount of dust on the filter in order to distinguish single particles.

## RESULTS AND DISCUSSION

### Mass concentrations

TSP mass concentrations were comprised between  $0.6 \text{ mg/m}^3$  for plant B and  $16 \text{ mg/m}^3$  for plant C.



PM fraction mass concentration

Table 1: Sampling results

Plant	Filter material	Average PM <sub>1</sub> (mg/m <sup>3</sup> )	Standard deviation PM <sub>1</sub> %	Average PM <sub>2.5</sub> (mg/m <sup>3</sup> )	Standard deviation PM <sub>2.5</sub> %	Average PM <sub>10</sub> (mg/m <sup>3</sup> )	Standard deviation PM <sub>10</sub> %
A, n=6	Q*	0.7	30	2.8	13	4.2	14
A, n=9	T**	2.0	33	3.1	25	4.0	18
A, average		1.5		3.0		4.1	
B, n=7	Q	0.2	47	0.3	45	0.4	46
B, n=4	T	0.1	80	0.2	50	0.2	40
B, average		0.2		0.3		0.3	
D, n=9	Q	2.0	31	2.7	28	4.0	34
D, n= 9	T	0.6	68	2.9	114	4.7	114
D, average		1.3		2.8		4.3	
C, n=9	Q	9.9	42	14.9	26	23.8	14
C, n=2	T	3.9	55	8.3	29	14.4	21
C, average		8.8		13.7		22.1	

: \*Quartz

\*\*PTFE

Table 2: Average PM fractions determined in the four plants

	Average concentration on the 4 plants (mg/m <sup>3</sup> )	Standard deviation on the 4 plants (mg/m <sup>3</sup> )
PM <sub>1</sub>	2.9	3.9
PM <sub>2.5</sub>	4.9	6.0
PM <sub>10</sub>	7.7	9.8

Differences in the distribution of particles within  $D < 1\mu\text{m}$  and  $D 1 - 2.5 \mu\text{m}$  fractions have been observed between samplings carried out using PTFE and quartz filter materials (see Table 1).

The PM 10 fraction varied between  $0.3 \text{ mg/m}^3$  in site A and  $22.1 \text{ mg/m}^3$  in site D. Levels measured in site A were in the range of the method quantification limits.  $\text{PM}_{2.5}$  represented between 61% and 100% of  $\text{PM}_{10}$ .

The finest fractions ( $D < 2.5 \mu\text{m}$ ) were the main contributors to the dust content in three out of four plants. In site D, the  $D 2.5 - 10 \mu\text{m}$  fraction was the main contributor. In all sampling sites, the  $D > 10 \mu\text{m}$  represented less than 5% of the dust concentrations.

## Chemical characterisation

### ➤ Trace elements

PAHs global concentrations in the four kilnsplants was below  $15.1 \text{ ng/m}^3$ . Naphtalene et phenantrene were the main contributors to the global PAHs concentrations determined in each plant.

The levels of concentrations of soluble chromium VI were below quantification limits for all plants. The levels of concentrations of non-soluble chromium VI were below quantification limits for three out of four plants. In site A, the concentration of non-chromium VI determined in the  $D < 1 \mu\text{m}$  fraction was  $0.24 \mu\text{g/m}^3$ , and close to blank levels for other fractions.

In three out of four plants, PAHs and trace metals were mainly present in the  $D < 1 \mu\text{m}$  fraction, concentrations close to blank levels could be observed in other fractions.

### ➤ Main contributors to the aerosol

The following table presents the molecular composition of the particles such as oxides and salts that could be identified from single particle analyses. These results were then used together with elements quantification in order to evaluate the main contribution of molecular compounds to the aerosol.

*Table 3: Molecular compounds identified by MEBE-EDS and Raman microspectrometry*

Diameter range	Plant A, Identified molecular compounds	Plant D, Identified molecular compounds
D > 10 $\mu\text{m}$	$\text{CaCO}_3$ , $\text{Fe}_2\text{O}_3$ , C graphite	-
D 2.5-10 $\mu\text{m}$	$\text{CaCO}_3$ , $\text{Fe}_2\text{O}_3$	$\text{CaCO}_3$ , C, $\text{K}_2\text{SO}_4$ , (Ca,K) $\text{SO}_4$
D 1-2.5 $\mu\text{m}$	$\text{CaCO}_3$ , $\text{Fe}_2\text{O}_3$ ,	$\text{CaCO}_3$ , C, $\text{K}_2\text{SO}_4$ , (Ca,K) $\text{SO}_4$ ,
D <1 $\mu\text{m}$	$\text{CaCO}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{TiO}_2$	$\text{CaCO}_3$

## Feedback from the sampling campaigns and recommendations

- Filter materials should be selected according to the chemical species to be determined.
- Carefull manipulation of filters after sampling is a crucial step of the process in order to guaranty good quality of the results. A lack of stability of impaction spots that can cause a bias when determining mass concentrations has indeed been observed .
- Although samplings for single particle analysis have been made very short (a few minutes), agglomeration of particles could not be avoided. This made the analysis of  $D > 10 \mu\text{m}$  impossible and  $2.5 \mu\text{m} < D < 10 \mu\text{m}$  analysis difficult.
- Trace elements determination may lead to results within the range of the quantification limits of the methods. This could not be solved by combining two samples into one analysis, due to the matrix effect that causes interferences during the analysis.
- The risk of particle bounce that can lead to an overestimation of fine fractions has been evaluated by MEBE analysis on  $D < 1\mu\text{m}$  and  $D 1 - 2.5 \mu\text{m}$  fractions. Good agreement with expected size distribution has been observed on these fractions (see Table 3).

Table 4: Range of size of particles observed by MEBE at INERIS

<u>Fraction</u>	<u>PTFE</u>				<u>quartz</u>			
	<u>Minimal diameter</u>	<u>Maximal diameter</u>	<u>Median</u>	<u>%*</u>	<u>Minimal diameter</u>	<u>Maximal diameter</u>	<u>Median</u>	<u>%*</u>
D < 1µm	0.1	4	0.6	87	0.2	3.5	0.6	85
1µm < D < 2.5 µm	0.3	5.2	1.1	97	0.2	3.2	0.9	99

## **CONCLUSION**

Measurement campaigns aiming at evaluating the use of manual impaction sampling prior to chemical and individual particle analysis and improving the knowledge of the French cement industry took place on four different cement plants in 2007 and 2008. These plants operated with a dry or semi-dry process equipped with either an ESP dust filter or bagfilters.

These campaigns led to a number of recommendations of use of the impaction allowing good quality results. These recommendations concerns filter manipulation, agreement between characterisation goals and sampling times, risk of particle bounces, choice of sampling materials, impact of sampling filter materials of PM fractions repartition.

Results from chemical analysis (elemental quantification) and single particle analysis (species identification) were used together in order to determine the main contribution of molecular compounds such as oxides to the aerosol. Trace elements could also be analysed although a number of them showed results in the range of the methods quantification limits.

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