

## **Demonstration of equivalence of PM automated monitoring methods: results of the 1st measurement campaign on a parisian urban background air quality station**

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# DEMONSTRATION OF EQUIVALENCE OF PM AUTOMATED MONITORING METHODS: RESULTS OF THE 1<sup>ST</sup> MEASUREMENT CAMPAIGN ON A PARISIAN URBAN BACKGROUND AIR QUALITY STATION

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## ABSTRACT

The present study summarizes the results of a measurement campaign conducted in Paris suburbs (Bobigny - 95) from January to March 2005, in the framework of Laboratoire Central de Surveillance de la Qualité de l'Air (LCSQA) activities. The main goal is to show that the methods tested (TEOM – FDMS from Thermo R&P and beta gauge MP101M-RST from Environnement SA) meet the Data Quality Objectives for PM<sub>10</sub> continuous measurements specified in the Air Quality Directive 99/30/EC, under conditions reflecting practical application in air quality monitoring networks. PM<sub>2.5</sub> continuous measurement feasibility has also been studied.

*Keywords:* Demonstration of equivalence, Data Quality Objective, EU Directives, automatic monitors

## INTRODUCTION

One of the objectives of the European Directive 96/62/EC (“Air Quality Framework Directive”, [1]) is to “assess the ambient air quality in Member States on the basis of common methods and criteria”. The European Air Quality Directives (“Daughter” Directives) relate to limit or target values for specified atmospheric pollutants (SO<sub>2</sub>, NO/NO<sub>x</sub>/NO<sub>2</sub>, PM<sub>10</sub>, CO, C<sub>6</sub>H<sub>6</sub>, O<sub>3</sub>, Heavy metals and PAH). These specify the principles of the Reference Methods (RM) to be used for the measurement of ambient concentrations. In addition, they specify Data Quality Objectives that have to be met for the performance of measurement in matter of uncertainty (i.e.: ± 25% for PM<sub>10</sub> in the region of the appropriate limit value [2]), using Reference Methods which are Standard Methods produced by European Committee for Standardization (CEN).

A Member State (MS) when implementing the Directives should use the Reference Methods, but the Directives allow MS the possibility to “use any other method which it can demonstrate results are equivalent to the Reference Method”. The European Commission has recently prepared a document describing principles and methodologies to be used for the demonstration of the equivalence of alternative (non-reference) measurement methods to the EN Standard Methods [3]. It is intended for use by laboratories to perform the tests relevant to the demonstration of equivalence of ambient-air measurement methods.

Concerning PM<sub>10</sub>, the 1<sup>st</sup> Daughter Directive specifies that measurements should be carried out using the Reference Method as defined in European Standard EN12341 [4]. This method presents some disadvantages (high operating costs, time resolution of measurement limited to 24 hours, Directive reporting requirements cannot be met). That is the reason why automated monitors such as Tapered Element Oscillating Microbalance (TEOM) or beta attenuation analysers) are widely used by Air Quality Monitoring Networks for measuring continuous concentrations of particulate matter. The principal disadvantage of automated methods is the requirement to hold the inlet and filter at a temperature above the atmospheric temperature, leading to potential loss of (semi)volatile species such as ammonium nitrate and so to differences with the Reference Method.

In order to avoid unrealistic data correction, french authorities have decided to study technical solutions developed by manufacturers aiming to reduce this loss of volatile components. The demonstration of the efficiency of such developments shall be done following the requirements of the European Document.

The present study summarizes the results of a measurement campaign conducted by INERIS and Ecole des Mines de Douai in Paris suburbs (Bobigny - 95) from January to March 2005, in the framework of Laboratoire Central de Surveillance de la Qualité de l’Air (LCSQA) activities. The main objective is to show that the candidate methods (CM) tested (TEOM – FDMS from Thermo R&P and beta gauge MP101M-RST from Environnement SA) meet the Data Quality Objectives for continuous measurements specified in the Air Quality Directive, under conditions reflecting practical application in air quality monitoring networks.

## METHODOLOGY

The experimental site is located at Bobigny (95) in an urban background area (Fig.1) and near an air pollution monitoring station from Airparif (Paris air quality network). The choice of site and time period of the year has been based on representativeness for typical conditions for which equivalence will be claimed, including possible episodes of high concentrations. These field tests shall be performed in which all methods are compared side-by-side (Fig.2).



Fig. 1: sampling site situation



Fig. 2: General view of apparatus

Concerning particulate matter  $PM_{10}$  and  $PM_{2.5}$ , the gravimetric reference used was a Partisol Plus 2025 sequential sampler (Thermo R&P) collecting on 47 mm diameter, 2  $\mu\text{m}$  pore size PTFE filters (Zefluor<sup>TM</sup> from Pall Corporation). The weighing procedure was conducted by INERIS according to requirements of European Standard EN 14907 [5], using a balance with a resolution of 10  $\mu\text{g}$  in a temperature ( $20 \pm 1^\circ\text{C}$ ) and humidity ( $50 \pm 5\% \text{RH}$ ) controlled weighing room. The 2 candidate methods were TEOM-FDMS ( $PM_{10}$  and  $PM_{2.5}$ ) and beta monitor MP101M-RST  $PM_{10}$ . All apparatus were duplicated et equipped with same US size-selective inlet. Sampling and monitoring series lasted 70 days for a total of 194 validated individual measurements. The objective was to collect a minimum of 40 duplicated pairs of measurement results each averaged over at least 24-hour per comparison.

## RESULTS

Figure 3 gives time series of  $PM_{10}$  concentrations observed during the campaign. It confirms that the monitoring method commonly used in AQ monitoring network (here TEOM) underestimates  $PM_{10}$  concentrations.

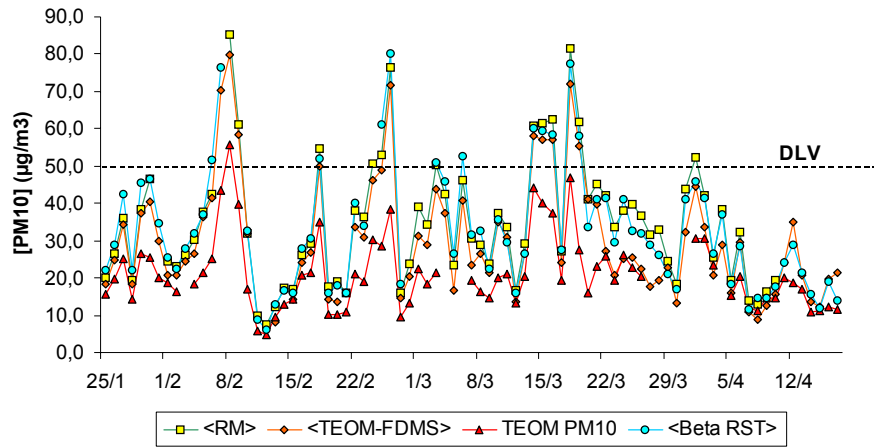


Fig. 3: PM<sub>10</sub> profiles at Bobigny

A good accordance of both new technologies with Reference Method is observed. 2 important points should be stressed:

- same exceedances number of daily limit value (50 µg.m<sup>-3</sup>) are detected by RM and CMs

- there is no need of correction factors or terms for CMs

A similar statement can be done for PM<sub>2,5</sub> measurements

Concerning PM<sub>10</sub>, all results obtained during the Bobigny campaign for both of candidate methods under the configuration used fulfil all criteria of equivalence demonstration procedure:

❶ datasets are suitable (at least 20% of the results are greater than 25 µg.m<sup>-3</sup> which is 50% of the daily limit value specified in the Daughter Directive)

❷ between-instrument uncertainty is satisfying (1,9 µg.m<sup>-3</sup> for MP-101M RST and 1,5 µg.m<sup>-3</sup> for TEOM-FDMS for performance criterion of 3 µg.m<sup>-3</sup> not to be exceeded), using equation (1) based on the differences of all 24-hour results of the instruments operated in parallel:

$$u_{bi}^2 = \frac{\sum_{i=1}^n (y_{i,1} - y_{i,2})^2}{2n} \quad (1)$$

Where:

$u_{bi}$  is between-instrument uncertainty

$y_{i,1}$  and  $y_{i,2}$  are the results of parallel measurements for a single 24-hour period  $i$

$n$  is the number of 24-hour measurement results.

- ③ orthogonal regression line equations are respectively  
 $MP-101M\ RST = 0,96 \times Reference + 1,09$  and  
 $TEOM-FDMS = 0,95 \times Reference - 1,69$

Slope and intercept are non significant according to statistical data treatment recommended in european document. Figure 4 and 5 give shape of orthogonal regression line:

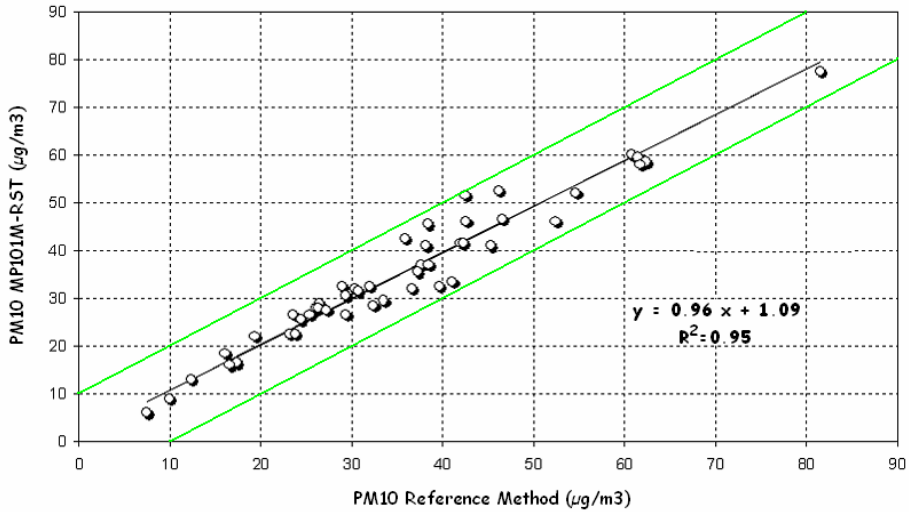


Fig. 4: Comparison of  $\beta$ -attenuation monitor with reference method (PM<sub>10</sub> 24h values)

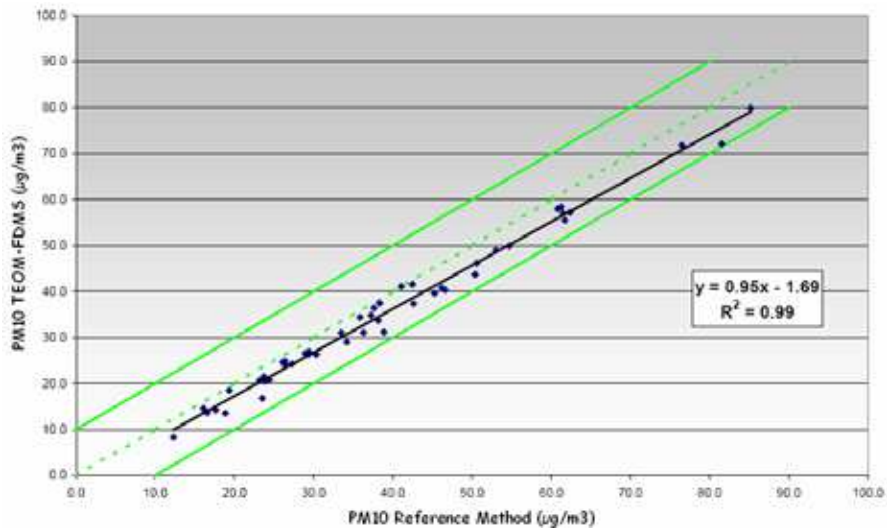


Fig. 5: Comparison of TEOM-FDMS with reference method (PM<sub>10</sub> 24h values)

④ expanded relative uncertainty at the level of daily limit value ( $50 \mu\text{g}\cdot\text{m}^{-3}$ ) observed during the campaign ( $\pm 13,2\%$  for MP-101M RST,  $\pm 17,6\%$  for TEOM-FDMS) meets data quality objective of  $\pm 25\%$  required by Directive 99/30/CE.

Concerning  $\text{PM}_{2.5}$ , similar good results are observed for TEOM-FDMS (In this assessment, a limit value for  $\text{PM}_{2.5}$  of  $35 \mu\text{g}\cdot\text{m}^{-3}$  has been assumed following european recommendations [6]):

① suitability of datasets (at least 20% of the results are greater than  $17,5 \mu\text{g}\cdot\text{m}^{-3}$  which is 50% of the assumed daily limit value)

② Satisfaction concerning between-instrument uncertainty ( $1,9 \mu\text{g}\cdot\text{m}^{-3}$  for TEOM-FDMS and  $0,9 \mu\text{g}\cdot\text{m}^{-3}$  for Reference Method for performance criterion respectively of 3 and  $2 \mu\text{g}\cdot\text{m}^{-3}$  not to be exceeded)

③ orthogonal regression line equation is

$$\text{TEOM-FDMS} = 1,03 \times \text{Reference} + 0,46$$

Figure 6 gives shape of orthogonal regression line:

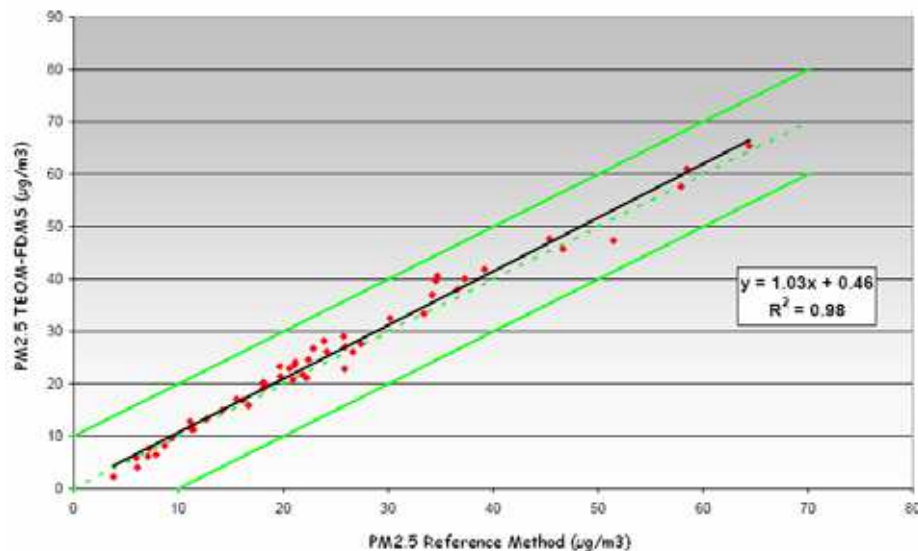


Fig. 5: Comparison of TEOM-FDMS with reference method ( $\text{PM}_{10}$  24h values)

④ expanded relative uncertainty at the level of the supposed daily limit value observed during the campaign ( $\pm 11,2\%$ ) meets data quality objective of  $\pm 25\%$  (assumed to be the same as the one required by Directive 99/30/CE for  $\text{PM}_{10}$ ).

## **CONCLUSION**

This first field result based on a specific protocol is quite encouraging for equivalence demonstration of TEOM-FDMS and  $\beta$ -attenuation monitor MP101M-RST for PM measurement. These results need to be confirmed in 3 other sites at minimum, with other composition of ambient air or meteorological conditions, in order to assume that equivalence for equipment tested is valid anywhere else under ambient conditions. A similar campaign performed at Marseille (South of France) from January to April 2006 has given similar satisfying results. The key point now is the establishment of the final report on the equivalence demonstration of these studied methods, to be submitted to the European Commission. A generalization of equivalence claims, based on sharing other european experiences conducted with similar analysers should be considered

## **ACKNOWLEDGEMENT**

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