



# Demonstration of Equivalence




## Demonstration of Equivalence of Methods for Measuring PM

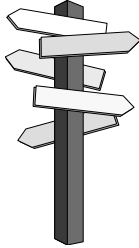
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## Roadmap of presentation



- ▶ Introduction
- ▶ Outline of equivalence demonstration
  - ▶ General procedure
  - ▶ Scope of equivalence claims
  - ▶ Test programmes
- ▶ Issues for particulate matter
- ▶ Examples
- ▶ Perspective


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## Introduction


- ▶ European Air Quality Directives (1999/30/EC, 2000/69/EC, 2002/3/EC, ?) specify
  - ▶ Limit values
  - ▶ Reference methods (RM)
  - ▶ Data Quality Objectives (DQOs) for specific measurement tasks
    - ▶ Expanded uncertainty (at limit value)
    - ▶ Time coverage
    - ▶ Data capture

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## Introduction

- ▶ Reference methods have been/are currently standardized and validated by CEN TC 264 Working groups against DQO
- ▶ However, a member state:  
“may use any other method which it can demonstrate gives results equivalent to the above method”
- ▶ Question: How ?



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## Introduction

- ▶ Subject of work of Working Group installed by European Commission:  
  
‘Guidance Report for Demonstration of Equivalence of Ambient Air Monitoring Methods’
- ▶ Published in 2005

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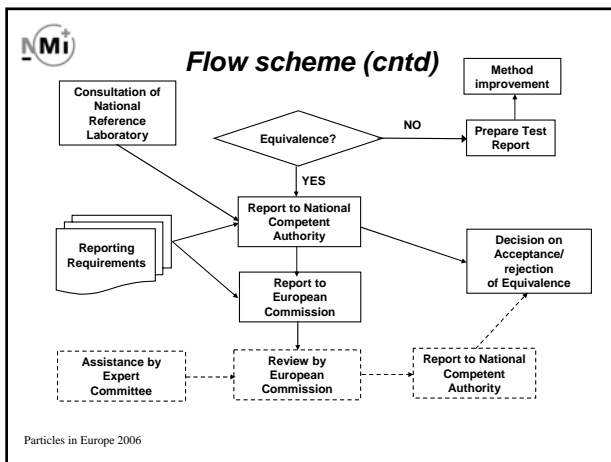
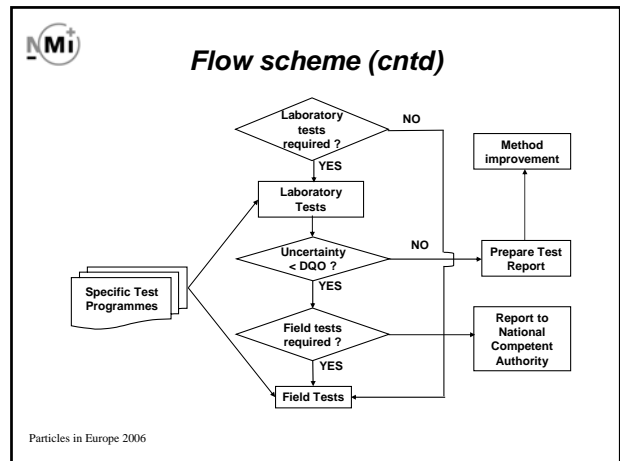
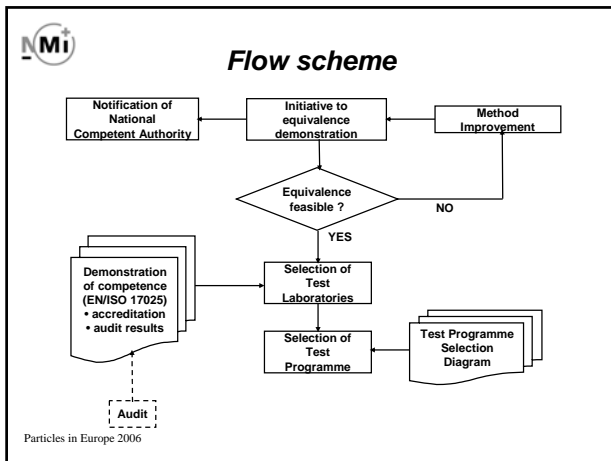




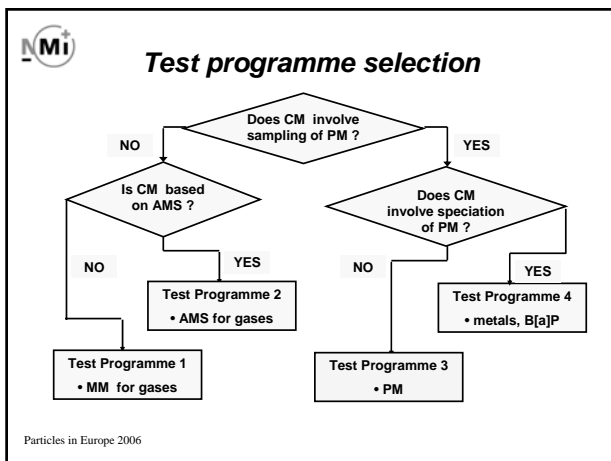
## General procedure

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# Demonstration of Equivalence



- Scope of equivalence claims**
- ▶ Equivalence can be granted for regional conditions
    - ▶ Composition of ambient air
    - ▶ Meteorology, geography
  - ▶ For reasons of economy of scale cooperation between regions/member states is recommended
  - ▶ Generalization of claims to other locations than those tested should be done with care
    - ▶ Particularly for PM !
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- Test and evaluation programmes**
- ▶ Consist of laboratory and field tests
  - ▶ Laboratory tests set up according to ISO-GUM
  - ▶ Field tests based on side-by-side comparison with Standard Method
    - ▶ Evaluation of uncertainty of Candidate Method based on orthogonal regression
    - ▶ Comparison of resulting expanded uncertainty with
      - ▶ Uncertainty from laboratory test programme (where relevant)
      - ▶ Uncertainty DQO
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## Particulate matter

- ▶ Special situation exists because of requirement for daily reporting (ex 1999/30/EC)
  - ▶ Use of automated methods inevitable !
- ▶ Problems occur related to semi-volatile fraction of PM
- ▶ Equivalence for AMS for PM may be granted after correction of AMS results

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## Issues for particulate matter

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## Laboratory tests

- ▶ Aimed at assessment of additional uncertainty caused by 'variation on a theme'
  - ▶ Use of filter-changer in instrument
  - ▶ Use of different weighing conditions
  - ▶ Use of different filter types ?

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## Automated filter-changer

```

    graph TD
      A[Establish worst-case conditions for filter storage in instrument] --> B[Collect ≥ 40 samples containing representative fractions of semi-volatiles]
      B --> C[Weigh samples under conditions prescribed in EN 14907]
      C --> D[Store samples in laboratory under worst-case conditions identified above (period, temperature)]
      D --> E[Reweigh samples]
      E --> F[Establish uncertainty contribution from largest mass difference found]
    
```

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## Weighing conditions

```

    graph TD
      A[Weigh ≥ 5 blanks from 2 batches under extremes of alternative conditions (low temperature/high relative humidity vs. high temperature/low relative humidity)] --> B[Collect ≥ 40 samples containing representative fractions of semi-volatiles]
      B --> C[Weigh samples under conditions prescribed in EN 14907]
      C --> D[Reweigh samples under proposed alternative conditions]
      D --> E[Establish uncertainty contribution from largest mass difference found]
    
```

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## Field tests

- ▶ Field tests based on side-by-side comparison with Standard Method
  - ▶ Under practical conditions covering 'amara' a wide range of possible conditions
    - ▶ Composition of ambient air
    - ▶ Meteorology
    - ▶ Geography
  - ▶ 4 measurement campaigns each giving a minimum of 40 valid results for the Candidate Method

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## Field tests

- ▶ **Acceptance criteria**
  - ▶  $\geq 20\%$  of data  $> 50\%$  of limit value
  - ▶ between-sampler uncertainty for Candidate Method  $\leq 3 \mu\text{g}\cdot\text{m}^{-3}$
  - ▶ between-sampler uncertainty for Standard Method  $\leq 2 \mu\text{g}\cdot\text{m}^{-3}$
  - ▶ orthogonal regression is applied to all 4 datasets individually, for data  $> 50\%$  of Limit Value, and for complete dataset
  - ▶ when slope  $\neq 1$  or intercept  $\neq 0$  at 95% confidence level: correction

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## Examples from Stimes PM<sub>10</sub> + EN 12341 comparisons

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## Stimes - filter stored in sampler

- ▶ Filters left in instrument for 14 days
- ▶ Maximum difference between samples from daily-changed and stored filters:
  - ▶  $12,3 \mu\text{g}\cdot\text{m}^{-3}$
  - ▶ additional uncertainty  $\pm 3,5 \mu\text{g}\cdot\text{m}^{-3}$
  - ▶ includes systematic differences between samplers (inlets, flows)
- related uncertainty generally  $\pm 2 \mu\text{g}\cdot\text{m}^{-3}$
- uncertainty contribution  $\pm 2,9 \mu\text{g}\cdot\text{m}^{-3}$

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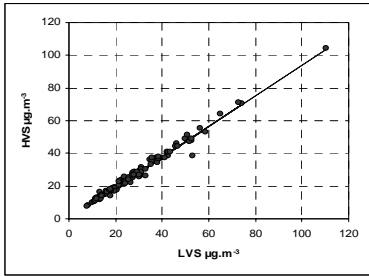
## Stimes - Glass-fibre vs Quartz-fibre

- ▶ Maximum difference between samples from HVS with GF and QF:
  - ▶  $8,3 \mu\text{g}\cdot\text{m}^{-3}$
  - ▶ additional uncertainty  $\pm 2,4 \mu\text{g}\cdot\text{m}^{-3}$
  - ▶ includes systematic differences between samplers (inlets, flows)
- related uncertainty generally  $\pm 2 \mu\text{g}\cdot\text{m}^{-3}$
- uncertainty contribution  $\pm 1,3 \mu\text{g}\cdot\text{m}^{-3}$

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## Stimes - LVS vs HVS



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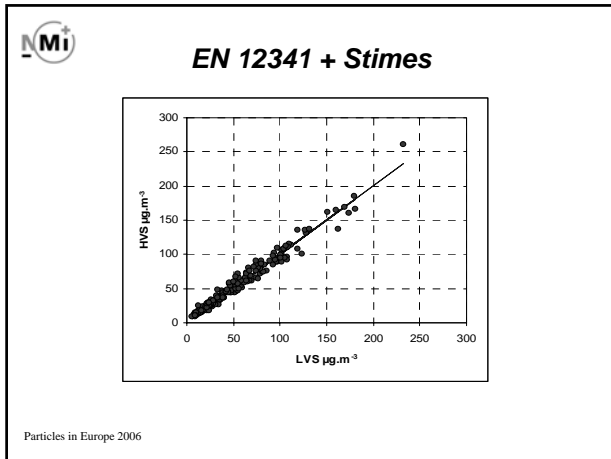
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## Stimes - LVS vs HVS

REGRESSION OUTPUT	
slope b	0.94
uncertainty of b	0.01 significant
intercept a	0.29
uncertainty of a	0.36
number of datapairs	114
r <sup>2</sup>	0.98
EQUIVALENCE TEST RESULTS	
random term	1.1 $\mu\text{g}/\text{m}^3$
bias at LV	-2.7 $\mu\text{g}/\text{m}^3$
combined uncertainty	2.9 $\mu\text{g}/\text{m}^3$
relative uncertainty	6% pass
ref between-sampler uncertainty	1.5 $\mu\text{g}/\text{m}^3$
limit value	50 $\mu\text{g}/\text{m}^3$

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### EN 12341 + Stimes

REGRESSION OUTPUT	
slope b	1.00
uncertainty of b	0.01
intercept a	0.22
uncertainty of a	0.49
number of datapairs	333
r <sup>2</sup>	0.98
EQUIVALENCE TEST RESULTS	
random term	5.1 µg/m <sup>3</sup>
bias at LV	0.3 µg/m <sup>3</sup>
combined uncertainty	5.1 µg/m <sup>3</sup>
relative uncertainty	10% pass
ref between-sampler uncertainty	2.0 µg/m <sup>3</sup>
limit value	50 µg/m <sup>3</sup>

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### EN 12341 + Stimes

REGRESSION OUTPUT	ISPRA	MADRID	COTTBUS	WIESBADEN
slope b	1.05	0.89	1.04	0.94
uncertainty of b	0.01 significant	0.01 significant	0.03	0.01 significant
intercept a	0.99	2.60	-1.06	0.29
uncertainty of a	0.48 significant	0.61 significant	2.44	0.36
number of datapairs	48	89	58	114
r <sup>2</sup>	0.99	0.99	0.97	0.98
EQUIVALENCE TEST RESULTS				
random term	0.6 µg/m <sup>3</sup>	2.8 µg/m <sup>3</sup>	7.5 µg/m <sup>3</sup>	1.1 µg/m <sup>3</sup>
bias at LV	3.7 µg/m <sup>3</sup>	-2.8 µg/m <sup>3</sup>	0.9 µg/m <sup>3</sup>	-2.7 µg/m <sup>3</sup>
combined uncertainty	3.8 µg/m <sup>3</sup>	3.9 µg/m <sup>3</sup>	7.6 µg/m <sup>3</sup>	2.9 µg/m <sup>3</sup>
relative uncertainty	8% pass	8% pass	15% fail	6% pass
ref between-sampler uncertainty	1.3 µg/m <sup>3</sup>	2.3 µg/m <sup>3</sup>	2.3 µg/m <sup>3</sup>	1.5 µg/m <sup>3</sup>
limit value	50 µg/m <sup>3</sup>	50 µg/m <sup>3</sup>	50 µg/m <sup>3</sup>	50 µg/m <sup>3</sup>

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### Perspective

- Gain experience with Guidance Report and approaches described
- Early 2007: organization of a workshop to exchange experiences with and ideas about the Guidance Report and its approaches

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### Perspective

- Comments/queries already received
  - Requirements for slopes and intercepts of regression equations for field tests too strict
  - Can pre-corrected AMS be defined as candidate method ?
  - Deletion of 1% of gravimetric results justifiable without technical reasons ?

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### Discussion ?

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