

## Artefacts in the sampling of nitrate studied in the “INTERCOMP” campaigns of EUROTRAC-AEROSOL

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### Abstract

Sampling of aerosol-nitrate can be problematic because of evaporative loss of the semi-volatile ammonium nitrate or adsorption of nitric acid gas. Such artefacts, which depend on filter type and ambient conditions, are not well documented for the filters in use in Europe and this was the reason to study these in a series of intercomparison trials. The trials were performed within the “INTERCOMP” programme of the AEROSOL subproject of EUROTRAC-2.

The major effort was a 2-week field campaign at the rural site of Melpitz, a village near Leipzig in eastern Germany (INTERCOMP2000). Samplers were used containing the most common filter types in use in Europe, i.e. quartz, Teflon, (mixed) cellulose ester and cellulose. The concentration of nitrate in PM<sub>2.5</sub>, mainly present as ammonium nitrate, was on average 3.3 µg m<sup>-3</sup>. The variability in the concentrations stemming from the samplers appeared to be rather constant: ± 0.5 µg m<sup>-3</sup> from the average of all samplers. The reason for the constant (but random) variability remains unexplained. Thus, the concentrations stemming from the samplers agreed very well at the average level with relative differences of 15% and less for higher concentrations. This is evidence that the influence of the mentioned artefacts was negligible. The absence is explained by extrapolation of results of tests on the artefacts in a laboratory setting (INTERCOMP99). It was found there that the loss of ammonium nitrate from Teflon and quartz filters is only substantial when temperatures are much higher than those during the field campaign. Cellulose and cellulose-acetate filters quantitatively collected both ammonium nitrate and nitric acid in the laboratory study, but in Melpitz measured nitric acid concentrations were too low to identify its adsorption. Possible artefacts due to adsorption of nitrous acid were negligible. We also used the laboratory information to evaluate the results of a further intercomparison (INTERCOMP98) in the Po-Valley, performed at much higher temperatures than at Melpitz. We found evidence of

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adsorption of nitric acid by cellulose filters and evaporational loss of aerosol-nitrate from quartz filters. For the conditions encountered during the campaign we parameterised the evaporational loss in a general way as a function of temperature, as follows. There is complete evaporation at temperatures exceeding 25 °C and full retention at temperatures less than 20 °C. At temperatures between 20 and 25 °C the retention is on average 50%, but with high variability.

A main conclusion from this study is that under central European conditions quartz is a suitable filter material for sampling nitrate as long as the temperature does not exceed 20 °C during sampling. Cellulose-type filters quantitatively collect aerosol nitrate and nitric acid, but negligible amounts of nitrous acid. Teflon filters were more vulnerable for evaporation losses than quartz. Indications for losses from Teflon below 10 °C (at Melpitz) were not obtained.

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## 1. Introduction

Nitrate is a dominant component of fine particulate mass in western and central Europe (Schaap et al., 2002). In summer, nitrate concentrations are consistently lower than in winter. This may be a real phenomenon but it can also be due to evaporation during sampling of the semi-volatile ammonium nitrate, the most dominant form in which nitrate is present in this part of Europe (Ten Brink et al., 1997; Schaap et al., 2002). The volatilisation artefact depends on the filter material and ambient meteorological conditions like temperature and relative humidity (Chow, 1995; Hering and Cass, 1999). There is a higher evaporative loss in summer, and the reason is that the evaporative tendency of ammonium nitrate strongly increases with temperature and is also higher in drier air. The evaporation artefact leads to serious underestimation of the true values, as illustrated in measurements in the Po-valley (Putaud et al., 2002), which will be further evaluated below.

Despite of the evaporation artefact the actual nitrate concentration can also be overestimated depending on the filter type. Cellulose type aerosol filters, in common use in Europe, may adsorb nitric acid and possibly nitrous acid gas which are thus assigned to aerosol nitrate (Spicer and Schumacher, 1979; Savoie and Prospero, 1982).

In the past, several studies were performed to investigate sampling artefacts by the use of different filter types and samplers (Appel et al., 1979; Eatough et al., 1988; Dasch et al., 1989; Harrison and Kitto, 1990; Hering and Cass, 1999; and others). Most of these studies have been performed in the US, where other filters are in use than in Europe. Those performed in northern Europe (Pakkanen et al., 1999) are of less relevance because the nitrate found there is mainly present in the form of stable compounds, like  $\text{NaNO}_3$  (Pakkanen et al., 1999).

In the study reported here we investigated the mentioned artefacts occurring during sampling of

aerosol nitrate. In the framework of the extensive INTERCOMP2000 campaign for comparison of aerosol sampling and establishing proper sampling tools a field intercomparison took place in Melpitz, near Leipzig. Melpitz is of particular interest because the station has a long record of nitrate data. The series shows a rapidly increasing importance of nitrate relative to sulphate concentrations in the course of the last decade (Spindler et al., 1999). Quartz filters are in use at the site. The campaign provided an opportunity to compare the data as obtained within the long-term record with those measured by the participants. Full details of the INTERCOMP2000 set-up and meteorology can be found elsewhere in this volume (Müller et al., 2004). We will only discuss the experimental set-up relevant for the nitrate sampling.

As a preparation for the field campaign a wind-tunnel study was performed in 1999 (Ten Brink et al., 2001). Here conditions like temperature, relative humidity and concentration of aerosol nitrate and related gases could be set. We present additional data and a full analysis of the results of the laboratory study. Furthermore, we make a full analysis of results of the Po-Valley study of which set-up and data are provided in Putaud et al. (2002). All of the campaigns were organised in the framework of the EUROTRAC-2 AEROSOL programme.

## 2. Experimental

### 2.1. INTERCOMP2000

#### 2.1.1. Site description

In the period of 4–13 April 2000 a field experiment was conducted at the Melpitz research station (latitude 51°32'N, longitude 12°54'E, altitude 87 m), located in the downstream plume of the Leipzig conurbation. A detailed description of the site and the meteorological situation during the campaign can be found in Müller et al. (2004) and Spindler et al. (2002). Conditions

during the campaign were quite cool and humid for the time of the year. The maximum temperature did not exceed 15 °C. Average daily temperatures were below 10 °C and the average relative humidity ranged between 67 and 88%.

### 2.1.2. Sampling methods

During the campaign four institutes used nine different samplers to collect aerosol samples for nitrate analysis or directly measured the nitrate content of the aerosol. The samplers, their acronyms and main features of the sampling methods are listed in Table 1 and described in detail below. As indicated, most of these were filter samplers with a PM2.5 or a PM10 pre-selector. In addition, three “stacked” filter-units (SFUs) and two low-pressure Berner impactors were operated. The filters used were Teflon, quartz fibre, polycarbonate, cellulose and mixed cellulose ester filters. A steam jet aerosol collector (SJAC) (Slanina et al., 2001) was used to measure nitrate with a 1-h time resolution. The filters and impactors were operated with a 12 or 24-h time resolution, starting at 8:00 a.m. for 24-h sampling and additionally at 8:00 p.m. for 12-h sampling. All available data were aggregated to 24-h values.

The IFT\_HV\_1 is a High Volume Digital (DHA80) sampler. The second high-volume sampler operated by IFT (IFT\_HV\_2) is a modified Sierra Anderssen-PM10 sampler, which has been used for monitoring purposes since 1992 (Spindler et al., 1999). Both systems were equipped with quartz fibre filters (Type MK 360, Munktell Filter, Sweden). The low-volume sampler

(IFT\_LV) is the Partisol 2000 Air Sampler (Rupprecht and Patashnik Co. Inc., USA) (Spindler et al., 2002). Daily samples of PM10, PM2.5 and PM1 were collected on Teflon filters (Millipore, Eschborn, Germany, Type 4700, 3 µm pore size). A 5-stage Berner low-pressure cascade impactor (IFT\_I) was also operated (Berner et al., 1979). A SJAC (Slanina et al., 2001), operated offline, was used to measure nitrate with a 1-h time resolution. The aerosol nitrate content was determined using a quarter of the filters from the IFT\_HV samplers or a half of the filters from the IFT\_LV samplers by standard ion chromatography procedure (Brüggemann et al., 2000).

The BTU\_HV sampler and sample analysis was identical to IFT\_HV\_1 (Wieprecht et al., 2001).

The TUV\_I instrument is an eight-stage low-pressure cascade impactor, type LPI 30 (Berner et al., 1979). The experimental and analysis procedures are described in Berner et al. (1998).

The three samplers used by UGent were Ghent PM10 SFU samplers (Maenhaut et al., 1994; Hopke et al., 1997). They were equipped with a Ghent PM10 inlet (Hopke et al., 1997), the aerosol was separated into two size fractions (PM2.0 and PM2-10) by sequential filtration through two 47mm diameter filters. The coarse filter was for all three samplers an 8 µm pore size, Apiezon-coated, Nuclepore polycarbonate filter. The fine filter was a Gelman Teflon filter (2 µm pore size) in UGent\_1; a Millipore mixed cellulose ester filter (acetate + nitrate), type SSWP04700 (3 µm pore size), in UGent\_2; and a Whatman 41 cellulose filter in

Table 1  
Overview of samplers used in Melpitz

Size	NR	Sampler	Filter/foil type	Flow (l min <sup>-1</sup> )	Extraction	Analysis	Blank <sup>c</sup> (µg m <sup>-3</sup> )
PM10	1	IFT_LV_2	Teflon	16.7	Water	IC	0.06
	2	IFT_HV_2	Quartz	1000	IC eluent <sup>d</sup>	IC	<0.02
	3	UGent_1 <sup>b</sup>	Polycarbonate	16.7	Water	IC	0.002
	4	UGent_2 <sup>b</sup>	Polycarbonate	16.7	Water	IC	0.002
	5	UGent_3 <sup>b</sup>	Polycarbonate	16.7	Water	IC	0.002
	6	IFT_SJAC	—	—	—	IC	—
PM2.5	7	BTU_HV	Quartz	500	Water	IC	<0.02
	8	IFT_LV_1	Teflon	16.7	Water	IC	0.06
	9	IFT_HV_1	Quartz	500	IC eluent <sup>b</sup>	IC	<0.02
	3	UGent_1 <sup>a</sup>	Teflon	16.7	Water	IC	0.002
	4	UGent_2 <sup>b</sup>	Mix. Cell. ester	16.7	Water	IC	0.2
5	UGent_3 <sup>c</sup>	Whatman 41	16.7	Water	IC	0.013	
PM1	10	IFT_LV	Teflon	16.7	Water	IC	0.06
Impactor	11	TUV_I	Aluminium	30	Water	IC	<0.002
	12	IFT_I	TEDLAR	75	Water	IC	<0.002

<sup>a</sup>PM2.0.

<sup>b</sup>Coarse filter, for PM10 the concentration derived from the fine and coarse filter have to be added up.

<sup>c</sup>With additional W41 backup filter during the latter half of the campaign.

<sup>d</sup>NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> buffer.

<sup>e</sup>Value is representative for a 24-h sampling period.

Table 2  
Experiment matrix and results of the wind-tunnel tests<sup>a</sup>

Design			Measured NO <sub>3</sub> concentration (µg m <sup>-3</sup> )					
Remarks			Denud	W41	CellAc	Qu	Teflon	SJAC
Dupl.	1	KNO <sub>3</sub> 10 µg m <sup>-3</sup>	9.2	6.8	12.2	11.8	9.2	9.2
	2	KNO <sub>3</sub> 10 µg m <sup>-3</sup>	8.7	7.9	8.7		8.5	8.5
	3	NH <sub>4</sub> NO <sub>3</sub> + HNO <sub>3</sub>	12.1	23.5	24.9	22.2	12.3	7.0
Dupl.	4	NH <sub>4</sub> NO <sub>3</sub> + HNO <sub>3</sub>	11.7	22.6	21.3		11.6	6.6
	5	overnight aerosol-free	-0.3	0.1	0.1	0.1	-0.0	<0.1
	6	HNO <sub>3</sub>	2.3	13.5	12.2	11.6	2.0	<0.1
Dupl.	7	HNO <sub>3</sub>	2.7	16.1	14.4		2.8	<0.1
	8	HNO <sub>2</sub>	0.4	0.8	0.5	0.6	0.0	<0.1
Dupl.	9	HNO <sub>2</sub>	0.5	1.3	0.5		-0.0	<0.1
	10	NH <sub>4</sub> NO <sub>3</sub> 20 µg m <sup>-3</sup>	21.0	16.6	20.1	21.2	15.1	16.6
Dupl.	11	NH <sub>4</sub> NO <sub>3</sub> 20 µg m <sup>-3</sup>	20.4	17.0	20.9		14.4	16.4
	12	NH <sub>4</sub> NO <sub>3</sub> 5 µg m <sup>-3</sup>	1.4	4.9	5.8	5.4	0.3	3.4
	13	NH <sub>4</sub> NO <sub>3</sub> 7 µg m <sup>-3</sup> (35°C)	12.9	14.3	16.0	1.9	0.1	8.9
Dupl.	14	NH <sub>4</sub> NO <sub>3</sub> 20 µg m <sup>-3</sup> (35°C)	32.3	34.5	35.8	10.5	1.2	26.2
	15	NH <sub>4</sub> NO <sub>3</sub> 20 µg m <sup>-3</sup> (35°C)	30.9	33.9	33.0		1.0	25.7
	15 + night	NH <sub>4</sub> NO <sub>3</sub> 20 µg m <sup>-3</sup> (35°C)	36.6	40.7	40.8	0.7	0.1	<0.1
Dupl.	17	KNO <sub>3</sub> 20 µg m <sup>-3</sup>	32.3	33.9	34.9	35.0	32.3	27.4
	18	KNO <sub>3</sub> 20 µg m <sup>-3</sup>	34.7	34.2	36.9		34.7	28.1

<sup>a</sup>The three standard filters used are denoted by: “W41”: Whatman-41 cellulose, “Qu”: quartz fiber, “Cell Ac”: cellulose acetate membrane. Sampling time was 2 h for each experiment. The detection limit for the various samplers is reflected in blank run 5. In runs 3,4,6–9 the measured nitric acid or nitrous acid gas concentration were very similar to the design value of 10 µg m<sup>-3</sup>. Experiments were performed at 21 °C and 50–60% RH unless stated otherwise. Dupl. indicates a duplicate run.

UGent\_3. From 7 April on, an additional Whatman 41 filter was used in the latter. Besides the actual samples, also 6 field blanks were collected with each of the three UGent samplers. Air was drawn through the field blanks for about 30 s. All samples were analysed for nitrate by ion chromatography (IC) (Maenhaut et al., 2002).

For all samplers the inlets and tubing (if any) were made from (passivated) aluminium or polyethylene. For a detailed description of the inlets we refer to the references given above. The residence time from inlet to filter was 1–3 s for all samplers. The chemical analyses were mostly performed in the laboratories of the participating institutes using very similar equipment and procedures. For an IC analysis done by one laboratory using the same equipment, procedure and staff the uncertainty was estimated to be about 10% (Brüggemann and Rolle, 1998). Annually, the laboratories involved take part in national and/or international intercomparison studies for qualifying their analytical data.

## 2.2. Laboratory study

In a laboratory setting tests were performed in a wind tunnel behind a large holding chamber in which both the

aerosol and the gases were generated. The sampling efficiency of potassium nitrate, as a conservative tracer, pure ammonium nitrate and a combination of ammonium nitrate and nitric acid gas were tested at various concentrations and temperatures (see Table 2). In addition, the adsorption of gaseous nitric and nitrous acid (HONO) was investigated. Filters of the same type as in INTERCOMP2000 were used. Ten Brink et al. (2001) describe the methods used to generate and sample the aerosol in detail. In this paper we report important (additional) data for Teflon filters (not presented earlier and of specific importance because of the use of this type of filter in INTERCOMP2000). The Teflon filter was the front filter in a filter pack (Behlen, 1996). The filter pack further consisted of a nylon back-up filter. The HONO test was specifically performed to test the assumed uptake of HONO by this material. Analysis of the filters for nitrate was performed by standard IC procedures (Behlen, 1996).

## 2.3. Po-Valley

The experimental set-up of INTERCOMP98 analysis procedures and site description are extensively described by Putaud et al. (2002) and Baltensperger et al. (2002).

### 3. Results and discussion

#### 3.1. INTERCOMP2000

In the analysis of the (nitrate) data from INTERCOMP2000 sulphate was considered to be the most conservative species. For comparison purposes the same procedure was followed for sulphate as for nitrate. In Fig. 1, the nitrate content of PM<sub>2.5</sub> at Melpitz is shown as obtained with the indicated samplers. The data show elevated concentrations from the 7th to the 12th of April, with maxima on the 8th and 11th. The average concentration of nitrate in PM<sub>10</sub>,  $4 \mu\text{g m}^{-3}$ , was close to the annual average at the site. During the campaign nitrate was mainly, at 81%, found in the PM<sub>2.5</sub> size range. During the campaign it was found that in continental influenced samples ammonium neutralizes about 87% of the nitrate and sulphate. The lowest ammonium to acid ratio, 73%, was found for 7 April,

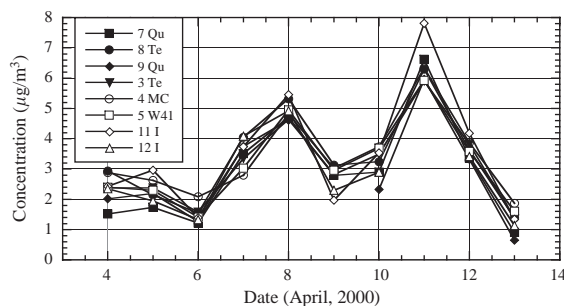


Fig. 1. Nitrate content of PM<sub>2.5</sub> during INTERCOMP2000. The numbers indicate the individual samplers (see Table 1) where the abbreviations denote its main feature: Te, teflon; Qu, quartz; MC, mixed cellulose ester; W41, Whatman41; and I, impactor.

when marine (influenced) air reached the measurement station. The ion balance shows that at that day nitrate was also present as  $\text{NaNO}_3$  predominantly in the hyper-micron range. Overall nitrate was predominantly found as ammonium nitrate during INTERCOMP2000, which is in accordance with the long-term data for this station (Spindler et al., 2003).

Average nitrate concentrations in PM<sub>2.5</sub> and PM<sub>10</sub> were calculated from all filter and impactor data. Since we could not identify any sampling artefacts, as discussed below, the averages serve as the reference values. The average nitrate concentration over the whole sampling period calculated from the averages of each sampler was  $4.0 \mu\text{g m}^{-3}$  with a 6% relative standard deviation and  $3.3 \mu\text{g m}^{-3}$  with a 6% relative standard deviation for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively. In Tables 3 and 4 the relative ratios between the samplers are shown. All samplers are within 15% of the average. Fig. 2 compares the data for PM<sub>10</sub> and PM<sub>2.5</sub> from the individual samplers to the reference values. The relative standard deviation of the average values for a single day ranges between 4% and 28% for PM<sub>10</sub> and between 6% and 30% for PM<sub>2.5</sub>. The highest standard deviations are found for the lowest concentrations, as a result of a quite constant absolute difference of about  $0.5 \mu\text{g m}^{-3}$  between samplers (see Fig. 3). Differences in the levels obtained with PM<sub>2.5</sub> samplers were slightly higher, which may be explained by the different cut-offs used ranging from 2.0 to  $3.5 \mu\text{m}$ .

The data obtained with cellulose or mixed cellulose ester filters fall well within the range of the data from the inert filters (Teflon and quartz). From the laboratory experiments, discussed below, we know that nitric acid gas is fully adsorbed by cellulose type filters. However, the concentration of nitric acid was so low relative to that of aerosol nitrate during the present campaign

Table 3

Ratio of the average concentration of nitrate and sulphate in PM<sub>10</sub> over the campaign to the mean of all samplers

PM <sub>10</sub>	IFT_LV	IFT_HV	UGent_1	UGent_2	UGent_3	TUV_I	IFT_I <sup>a</sup>	SJAC
NO <sub>3</sub>	1.02	0.89	1.01	1.06	1.01	1.01	0.97	1.14
SO <sub>4</sub>	1.10	0.95	1.06	1.01	0.98	1.01	1.02	1.18

<sup>a</sup>Without the 11th.

Table 4

Ratio of the average concentration of nitrate and sulphate in PM<sub>2.5</sub> over the campaign to the mean of all samplers

PM <sub>2.5</sub>	IFT_LV	BTU_HV	IFT_HV <sup>a</sup>	UGent_1	UGent_2	UGent_3	TUV_I	IFT_I <sup>b</sup>
NO <sub>3</sub>	1.03	0.90	0.88	0.97	1.04	0.98	1.07	0.94
SO <sub>4</sub>	1.04	1.14	1.03	0.97	0.93	0.88	1.04	0.92

<sup>a</sup>Without the 9th.

<sup>b</sup>Without the 11th.

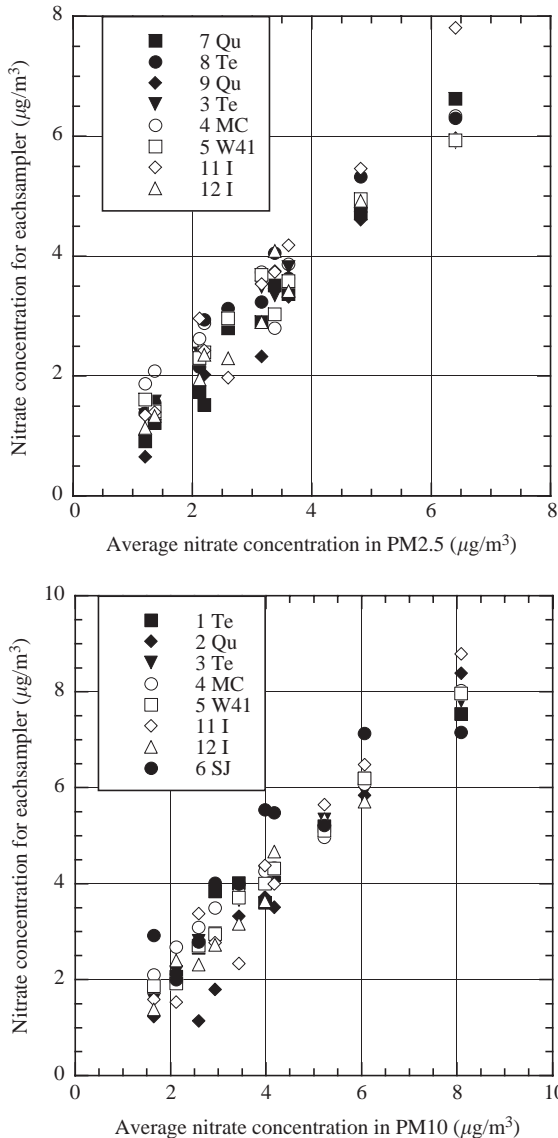


Fig. 2. Comparison between the nitrate concentrations obtained from the individual samplers and the average nitrate concentration in PM<sub>2.5</sub> (upper panel) and PM<sub>10</sub> (lower panel). The numbers indicate the individual samplers (see Table 1) where the abbreviations denote its main feature: Te, teflon; Qu, quartz; MC, mixed cellulose ester; W41, Whatman41; I, impactor and SJ, SJAC.

(Acker et al., 2004, this issue) that its interference is small. Therefore, nitric acid does not give rise to significantly different values from those obtained with the inert filters on which nitric acid does not adsorb. The same conclusion is valid in case inlets or tubing have acted as a denuder (by stripping the nitric acid from the air).

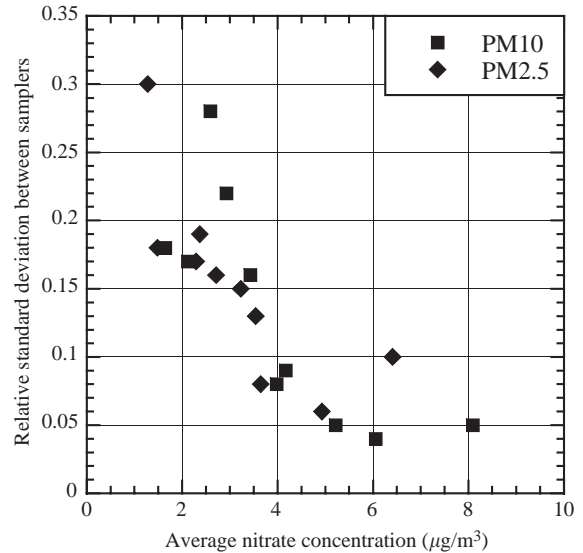


Fig. 3. Relative standard deviation in the average of all samplers for PM<sub>2.5</sub> and PM<sub>10</sub> per day.

On average, the SJAC data for PM<sub>10</sub> seem to be slightly higher than the other data. Because the non-volatile sulphate shows the same feature (see Table 3), we conclude that this finding cannot be interpreted as a loss of nitrate by evaporation from the filters. Additionally, an absence of volatilization is in good agreement with the comparability of the data from the inert and cellulose filters. The laboratory intercomparison showed that no volatilization occurred from the latter, and we conclude that evaporation from the inert filters was not significant. In the absence of a systematic difference between samplers, artefacts can almost certainly be excluded as the reason for the rather constant differences between the concentrations determined with the different samplers. Also, the blank values for nitrate (Table 1) were much lower than the observed variability. In addition, the variability between samplers with different cut-off's or sampling volumes and between filter samplers and impactors appears to be random. Therefore, the explanation for the observed constant variability remains unclear.

Ferm et al. (1988) compared different total nitrate samplers. For daily average total nitrate concentrations relative standard deviations lower than 15% were found for different laboratories using the same sampling technique. At the low end of the concentration range ( $<2\mu\text{g}/\text{m}^3$ ) standard deviations were significantly higher. When each laboratory used their own technique very similar results were found. These findings are in good agreement with the data in our study. The same applies for a study by Harrison and Kitto (1990).

### 3.2. Laboratory study

Below we present additional data and a full analysis of the laboratory study. The first step was to test the collection efficiency of the filters for submicron aerosol with stable potassium nitrate. It was found that even the Whatman 41 filter sampled close to 100%. With the semi-volatile ammonium nitrate, sampled at an air temperature of 21 °C, the quartz filter sampled as much as the reference sampler. However, only 75% of the nitrate was collected on the front Teflon filter of the filter pack. At an elevated air temperature of 35 °C, less than 30% of the nitrate was sampled on the quartz and almost none on the Teflon filter. These differences are due to evaporation of ammonium nitrate after collection. The reason is that the aerosol sampled on the filters is not in equilibrium with the associated gases because the time between generation and arrival at the filters is too short to establish this equilibrium (under equilibrium conditions at 35 °C,  $46 \mu\text{g m}^{-3}$  of ammonium nitrate will be present in the gas phase as ammonia and nitric acid (Seinfeld and Pandis, 1998)). The presence of this disequilibrium is indicated by the measured low concentrations of nitric acid, which were less than 10% of the equilibrium value. In contrast to the quartz and Teflon filters the cellulose-type filters quantitatively retained the nitrate.

In the interference test with nitric acid gas, the nitrate concentrations found on the cellulose-type filters were similar to the nitric acid concentration measured with the gas-denuders. This shows that these filter types quantitatively collect nitric acid. The retention appeared to be in the form of ammonium nitrate. This is probably due to neutralization of the nitrate on the filter by  $\text{NH}_3$ , which was present at a continuous background level. Additional tests at a later date showed that nitric acid is also retained on cellulose filters in the absence of ammonia. A marginal amount of nitrate was found on the Teflon filter. In contrast, the other inert material, quartz, quantitatively collected the nitric acid, in the form of ammonium nitrate. This ammonium nitrate was apparently formed on the filter in a reaction of the nitric acid and the mentioned free ammonia in the system. In the runs with both ammonium nitrate and nitric acid the Teflon filters only collected ammonium nitrate, whereas the quartz sampled also nitric acid, showing the very complex behaviour of quartz towards nitrate. HONO gave an almost negligible interference, also on the nylon back-up filter in the filter-pack.

A crucial test was that to measure the retention of ammonium nitrate in loaded filters when aerosol-free air of 35 °C was passed through the filters for an extended period. No evaporation was observed from the cellulose-type filters. The nitrate was retained as ammonium nitrate. The quartz and Teflon filters showed virtually complete evaporation, see Table 2.

### 3.3. Po-Valley

During the late spring of 1998 an intercomparison of three samplers took place in the Po-Valley within a larger field campaign (PIPAP0). Some results of this campaign have already been reported (Putaud et al., 2002; Baltensperger et al., 2002). We provide a full evaluation of the differences observed for the nitrate concentrations as obtained with the quartz filters, the Whatman 41 cellulose filters and the artefact free on-line method. Fig. 4 compares the results of the cellulose filter measurements (Putaud et al., 2002) with those obtained by the WEDD/AC system (Baltensperger et al., 2002). For this purpose, the measurements from the WEDD/AC system (20 min resolution) were integrated for comparison with the longer sampling time of filters (4–7 h resolution), correcting the filter data for the  $\text{HNO}_3$  artefact (by subtracting the  $\text{HNO}_3$  data as measured with the WEDD/AC from the filter data). Both methods show good agreement with respect to the nitrate concentration and exhibit a correlation coefficient  $R^2=0.94$ , with 6% more nitrate determined on the filters. This confirms the ability of cellulose filters to quantitatively sample ammonium nitrate even at elevated temperature (temperatures ranged between 18 and 30 °C). At low concentration ranges there seems to be a small offset between the samplers with slightly more nitrate found on the WEDD/AC. Although the reason is unclear to us, we speculate that at low loadings the W41 may not fully capture all PM. In addition, the uncertainty of a single measurement and therefore that of the correction for nitric acid are highest at low concentration ranges contributing to the variability in the comparison.

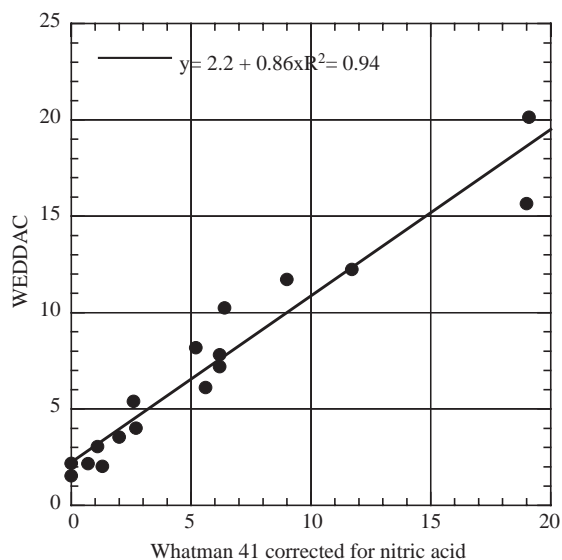


Fig. 4. Concentration of nitrate ( $\mu\text{g m}^{-3}$ ) as sampled on a Whatman 41 filter (corrected for  $\text{HNO}_3$ ) compared to the WEDD/AC.

Using this information, we analysed the evaporation artefact of quartz filters as a function of (average) temperature during the sampling period, by classifying the temperature into three regimes. We corrected the Whatman 41 data for the contribution of nitric acid to obtain the actual aerosol nitrate concentration using measured concentrations of nitric acid (Baltensperger et al., 2002). In Fig. 5 the nitrate concentrations obtained with the quartz filters are compared with those obtained with the cellulose filters. It can be clearly observed that the differences between the two samplers were highest for the highest temperatures. The average concentration ratios between the samplers are given in Table 5 for three temperature intervals (we excluded one obvious outlier). It was found that at temperatures higher than 20 °C substantial or complete loss of ammonium nitrate occurs from the quartz filters.

### 3.4. General discussion and implications for monitoring

#### 3.4.1. Cellulose-type filters and adsorption artefact

In Europe cellulose filters are in use in the EMEP network. From the present study we conclude that these

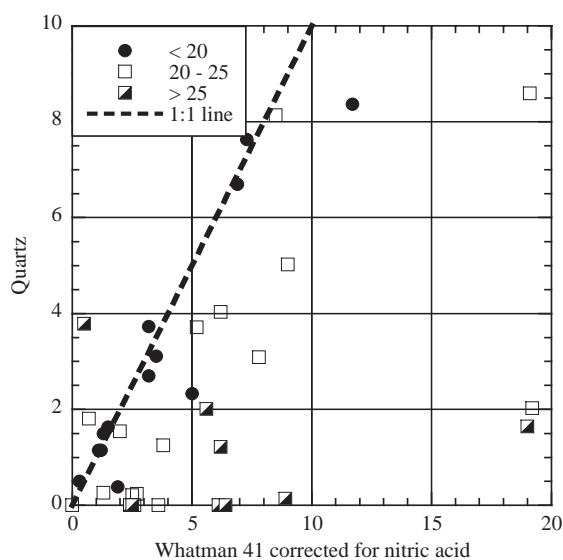


Fig. 5. Concentration of nitrate ( $\mu\text{g m}^{-3}$ ) as sampled on a quartz filter compared to that on a Whatman 41 filter (corrected for  $\text{HNO}_3$ ).

Table 5

Po-Valley: ratio of nitrate on Quartz to Whatman41 filters, with and without correction for nitric acid absorption by W41

Temperature (°C)	Raw data	$\text{HNO}_3$ corrected
< 20	0.58	0.93
20–25	0.29	0.41
> 25	0.07	0.08

filters are samplers of total nitrate. This conclusion, viz., that cellulose-based filters quantitatively collect nitric acid, is substantiated by earlier studies by Appel et al. (1979), Spicer and Schumacher (1979) and Mehlmann (1986), who showed that the capacity of retaining nitric acid on cellulose filters is limited. However, the loads measured in the laboratory and in the field experiments reported here are (much) lower than the saturation limit.

#### 3.4.2. Evaporation artefact

Underestimation of the nitrate concentration with Teflon filters is a well-documented phenomenon (Appel et al., 1979; Chow, 1995; Hering and Cass, 1999), but less so with quartz for which few data exist on the temperature dependence of the evaporation artefact. In Fig. 5 we summarize the information on the evaporation artefact with quartz filters obtained in this study. In INTERCOMP2000 we did not find a measurable evaporation artefact. Its absence was explained by the relatively low temperature and high relative humidity encountered during the campaign. These conditions should be associated with very low concentrations of the gases associated with the semi-volatile ammonium nitrate. Indeed, the measured nitric acid concentrations were low (Acker et al., 2004, this issue). At temperatures exceeding 25 °C during the Po-Valley campaign and in the wind tunnel complete loss of nitrate was observed from quartz filters, whereas a partial loss was observed between 20 and 25 °C. These results are in agreement with those of Eatough et al. (1988), who also observed considerable losses in the afternoon with temperatures exceeding 20 °C. Below 20 °C no significant evaporation was observed. It is suggested that losses during a 24 h sampling period is not only a function of ambient conditions and sampling apparatus, but also of the sampling strategy. When filters are changed in the morning, losses may have occurred at the higher temperatures in the afternoon of the previous day whereas at night nitrate is sampled quantitatively. When filters are changed in the afternoon or evening, nitrate sampled during the night might be lost when temperatures rise during the day. Such seemingly minor details, together with the type of filter material used and length of sampling lining in which nitric acid may be lost, should in reality be spelled out when nitrate measurements are being reported.

## 4. Conclusions

In this study we report on the comparability of nitrate measurements as studied in three intercomparison campaigns. During the campaign in Melpitz the nitrate concentrations obtained from the different samplers compared well. Evaporation artefacts were not identified, which was attributed to the stability of ammonium



nitrate at the low ambient temperatures and high relative humidity. Adsorption of nitric acid to cellulose filters could not be identified, although it was found in the wind tunnel intercomparison experiment. There it was established that cellulose-type filters sample the sum of particulate nitrate and nitric acid. Artefacts in the sampling of ammonium nitrate with quartz filters were complex. Evaporation only occurred at the higher temperature of 35 °C. Teflon filters were more vulnerable for evaporation losses than quartz. Using this laboratory knowledge the data from a third intercomparison campaign in the Po-Valley, in 1998, were evaluated. We found clear evidence of adsorption of nitric acid by cellulose filters and evaporational loss of aerosol-nitrate from the quartz filters used. For the conditions encountered during the campaigns we could parameterize the latter loss as a function of temperature, as follows. There is complete evaporation at temperatures exceeding 25 °C and full retention at temperatures less than 20 °C. At temperatures between 20 and 25 °C the retention is on average 50%, but with high variability.

A main conclusion from this study is that under central European conditions quartz is a suitable filter material for sampling nitrate as long as the temperature does not exceed 20 °C during sampling. Cellulose-type filters quantitatively collect nitric acid and particulate ammonium nitrate, but negligible amounts of nitrous acid. A final remark is that seemingly minor details like the time of filter change, type of filter material and length of the sampling line, should in reality be spelled out and tested with respect to effect on the sampling before nitrate measurements are being made and reported.

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