2　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 two-week field campaign at the rural site, Melpitz, near Leipzig in eastern Germany, with samplers containing the most common filter types in use in Europe. The concentration of nitrate, present as ammonium nitrate, was on average 4 µg/m^3. The concentrations stemming from the samplers agreed very well, with relative differences at the average level, of 10 % 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. 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. None of the filters adsorbs gaseous nitrous acid, which was present at substantial levels. We also used the laboratory information to evaluate the results of an intercomparison in the Po-Valley, performed at much higher temperatures than at Melpitz. We found evidence of adsorption of nitric acid by cellulose filters and evaporation losses of aerosol-nitrate from quartz filters. We parameterised the extend of the evaporation in a general way as a function of temperature. 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 quartz is a suitable filter material for sampling nitrate as long as the temperature does not exceed 20 °C during sampling. Cellu-lose type filters quantitatively collect nitric acid, but negligible amounts of nitrous acid.

2.1 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, the reason being a larger evaporative tendency of ammonium nitrate with increasing temperatures and with 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, commonly used 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 $NaNO_3$ (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 in Müller et al., (2003). 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. Here conditions like temperature, relative humidity and concentration of aerosol nitrate and related gases could be controlled. Furthermore, the results of the already mentioned Po-Valley study will be discussed in this paper. All of the campaigns were organised in the framework of the EUROTRAC-2 AEROSOL programme.

Table 2.1 Overview of samplers used

Size	Nr	Sampler	Filter/Foil type	Flow (l/min)	Extraction	Analysis
PM10	1	IFT_HV_2	Quartz	1000	Water	IC
	2	IFT_LV_2	Teflon	16.7	Water	IC
	3	Ugent_1[a]	Nuclepore	16.7	Water	IC
	4	Ugent_2[a]	Nuclepore	16.7	Water	IC
	5	Ugent_3[a]	Nuclepore	16.7	Water	IC
	6	IFT_SJAC	-		Water	IC
PM2.5	7	BTU_HV	Quartz	500	Water	IC
	8	IFT_HV_1	Quartz	500	Water	IC
	9	IFT_LV_1	Teflon	16.7	Water	IC
	3	Ugent_1[b]	Teflon	16.7	Water	IC
	4	Ugent_2[b]	Mix. Cell. ester	16.7	Water	IC
	5	Ugent_3[bc]	Whatman 41	16.7	Water	IC
PM1	10	IFT_LV	Teflon	16.7	Water	IC
Impactor	11	IFT_I	TEDLAR	75	Water	IC
	12	TUV_I	Aluminium	30	Water	IC

[a] PM2.0, [b] coarse filter, for PM10 the concentration derived from the fine and coarse filter have to be added up, [c] with additional W41 backup filter during the latter half of the campaign

2.2   Experimental

2.2.1   INTERCOMP2000

Site description and meteorological conditions

In the period of 4 to 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. (2003). Conditions during the campaign were quite cool and humid for the time of the year. The maximum temperature did not exceed 15 °C. Daily average temperatures were all below 10 °C and the average relative humidity ranged between 67 and 88 %.

Sampling methods

During the campaign four institutes used twelve 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 2.1 and described in detail below. As indicated most of these were filter samplers with a PM2.5 and a PM10 pre-selector. In addition, three "stacked" filter-units (SFU) and two

low pressure Berner impactors were operated. The filters were either inert (Teflon, Quartz fibre or polycarbonate) or of a cellulose-based material (cellulose or a mixed cellulose ester). A Steam Jet Aerosol Collector (SJAC) (Slanina et al., 2001) was used to measure nitrate with a one-hour time resolution. The filters and impactors were operated with a 12 or 24-hour time resolution, starting at 8:00 a.m. for 24-hour sampling and additionally at 8:00 p.m. for 12-hour sampling. All available data were aggregated to 24-hour values.

The IFT_HV_1 is a High Volume Digitel (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 (25.4 x 20.3 cm, Type MK 360, Munktell Filter, Sweden). The low volume sampler 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 Steam Jet Aerosol Collector (SJAC) (Slanina et al., 2001), operated offline, was used to measure nitrate with a one-hour time resolution. The aerosol nitrate content was determined from a quarter of the HV filters or a half of the LV filters, respectively, 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 a nine-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 Gent PM10 stacked filter unit (SFU) samplers (Maenhaut et al., 1994; Hopke et al., 1997). They were equipped with a Gent PM10 inlet (Hopke et al., 1997), the aerosol was separated into two size fractions (PM2.0 and PM2-10) by sequential filtration through two 47-mm diameter filters. The coarse filter was for all three samplers an 8 micron pore size, Apiezon-coated, Nuclepore polycarbonate filter. The fine filter was a Gelman Teflon filter (2 micron pore size) in Ugent_1; a Millipore mixed cellulose ester filter (acetate + nitrate), type SSWP04700 (3 micron pore size), in Ugent_2; and a Whatman 41 cellulose filter in Ugent_3. From April 7 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 seconds. All samples were analysed for nitrate by ion chromatography (IC). Each sample was placed in a 15 mL polystyrene tube and extracted with 10 mL Milli-Q water in an ultrasonic bath (60 min). The IC analyses were done with a DIONEX 4500i chromatograph, with a conductometric detector, an AG12A guard column, an AS12A analytical column, an ASRS auto-suppressor with external water mode and a PC-based AutoIon (AI-450) data acquisition and analysis system. The eluent was 2.7 mM sodium carbonate / 0.3 mM sodium bicarbonate (isocratic). Injection of the samples was done manually using a 100-µL sample loop.

Table 2.2 Experiment matrix and results in the wind-tunnel tests.

The abbreviations used for the different methods are:

"Paper":   Whatman-41 cellulose

"Qrz":   Quartz fiber

"CA":   Cellulose acetate membrane

"DD":   Denuder difference method

The detection limit for the various samplers is reflected in blank run 5. In runs 3,4,6-9 the measured nitric acid gas concentration was very similar to the design value of 10 $\mu g\ m^{-3}$.

Experiment design			Measured nitrate NO3 ($\mu g\ m^{-3}$)					
			DD	Paper	CA	Qrz	Teflon	SJAC
	1	KNO_3 10 $\mu g/m^3$	9.2	6.8	12.2	11.8	9.2	9.2
duplo	2	KNO_3 10 $\mu g/m^3$	8.7	7.9	8.7		8.5	8.5
	3	NH_4NO_3+HNO_3	12.1	23.5	24.9	22.2	12.3	7.0
duplo	4	NH_4NO_3+HNO_3	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_3	2.3	13.5	12.2	11.6	2.0	<0.1
duplo	7	HNO_3	2.7	16.1	14.4		2.8	<0.1
	8	HNO_2	0.4	0.8	0.5	0.6	0.0	<0.1
duplo	9	HNO_2	0.5	1.3	0.5		-0.0	<0.1
	10	NH_4NO_3 20$\mu g/m^3$	21.0	16.6	20.1	21.2	15.1	16.6
duplo	11	NH_4NO_3 20$\mu g/m^3$	20.4	17.0	20.9		14.4	16.4
	12	NH_4NO_3 5$\mu g/m^3$	1.4	4.9	5.8	5.4	0.3	3.4
	13	NH_4NO_3 7$\mu g/m^3$ (35°C)	12.9	14.3	16.0	1.9	0.1	8.9
	14	NH_4NO_3 20$\mu g/m^3$ (35°C)	32.3	34.5	35.8	10.5	1.2	26.2
duplo	15	NH_4NO_3 20$\mu g/m^3$ (35°C)	30.9	33.9	33.0		1.0	25.7
15+ night	16	NH_4NO_3 20$\mu g/m^3$ (35°C)	36.6	40.7	40.8	0.7	0.1	
	17	KNO_3 20$\mu g/m^3$	32.3	33.9	34.9	35.0	32.3	27.4
duplo	18	KNO_3 20$\mu g/m^3$	34.7	34.2	36.9		34.7	28.1

2.2.2   Laboratory intercomparison

The tests in the laboratory-based INTERCOMP99 have been described elsewhere (Ten Brink et al., 2001), and the relevant parameters are summarised here (Table 2.2). Tests were performed in a wind tunnel behind a large holding chamber in which the aerosol was generated. A series of filter samplers with different filter types were compared. Non-volatile potassium nitrate was used as a reference material. The sampling efficiency of pure ammonium nitrate and a combination of ammonium nitrate and nitric acid gas were tested, at various concentrations and temperatures. In addition, the adsorption of gaseous nitric and nitrous acid (HONO) was investigated. The typical sampling time was 2 hours to allow for duplicate tests.

Samplers

Filters of the same type as in INTERCOMP2000 were used, but were placed in open-face filter holders without inlet tubing to prevent losses of nitric acid in this tubing. A denuder difference method (Behlen, 1996) served as the reference (artefact-free) collection method. The first filter in the filter pack was Teflon, which allowed for the assessment of the sampling characteristics of this material. The filter pack further consisted of a nylon back up filter and was used in combination with a separate sodium chloride coated denuder. The SJAC was also present. This served two purposes: first the SJAC was tested against the other methods and, secondly, it was used to follow, on-line, the concentration of nitrate and ammonium and to check the concentration of the associated gases in the set-up phase of the test.

Comparability of the analysis procedures was good, and "field" blanks were negligible compared to values obtained with actual sampling of aerosol-nitrate.

Aerosol and gas generation

Particle-free ambient air, which was typically at temperature of 21 °C and a relative humidity between 50 and 60 %, was pumped through the chamber and wind-tunnel at a flow of 15 m^3/min. This rate allows for the use of a variety of samplers in parallel. Aerosol nitrate and nitric acid were produced by nebulizing nitrate and nitric acid solutions, respectively. The generated droplets rapidly dried when the small aerosol stream was added to the main flow. The resulting particles had a size and a mass concentration comparable to those in the atmosphere. Stability in the generation is an important parameter because evaporative loss of ammonium nitrate is also a function of filter loading (Chow, 1995). The concentration of the aerosol during a run was therefore followed with a time resolution of one minute with both an optical sizer (LAS-X) and an integrating nephelometer (Ten Brink et al., 2000) and it was found that short-time volume/mass fluctuations were less than 5 %.

The nitric acid production was tested with an automated wet-denuder (Slanina et al., 2001). Wall losses of nitric acid in the large system appeared to be negligible. It was also checked that the concentration of nitric acid and the aerosols was homogeneous over the inner central half of the exit plane where the samplers were placed.

HONO was generated by a method developed at MPI, Hamburg (Behlen, 1996). The concentration and the stability of HONO generation were followed by a NO$_x$-monitor. The concentration of this gas decreased with some 25 % over time, but there were no short-time fluctuations.

2.2.3 Po-valley

The experimental set-up, analysis procedures and site description are extensively described by Putaud et al. (2002) and Baltensperger et al. (2002).
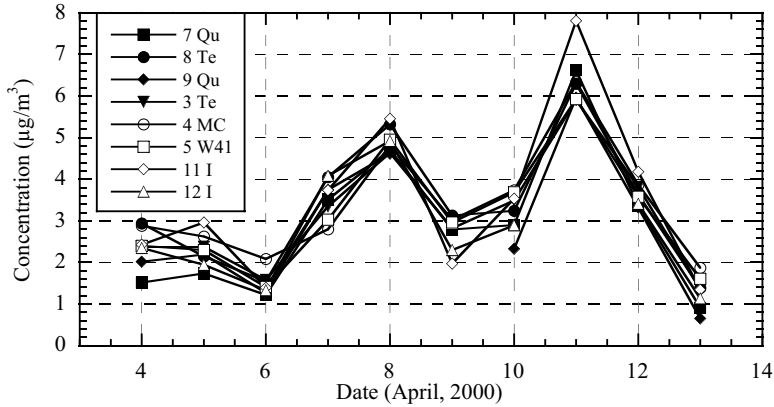
Figure 2.1 Nitrate content of PM2.5 during INTERCOMP2000. The numbers indicate the individual samplers (see Table 2.1) where the abbreviations denote its main feature: Te = Teflon, Qu = Quartz, MC = Mixed Cellulose ester, W41 = Whatman41, and I = Impactor.

2.3   Results and discussion

2.3.1   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 Figure 2.1, the nitrate content of PM2.5 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 PM10, 4 $\mu g/m^3$, was close to the annual average at the site. During the campaign nitrate was mainly, at 81 %, found in the PM2.5 size range. Average nitrate concentrations in PM2.5 and PM10 were calculated from all filter and impactor data and served as reference values. The average nitrate concentration over the whole sampling period calculated from the averages of each sampler was 4.0 $\mu g/m^3$ with a 6 % relative

Table 2.3 Ratio of the average concentration of nitrate and sulphate in PM10 over the campaign to the mean of all samplers, # without the 11th

PM10	IFT_LV	IFT_HV	Ugent_1	Ugent_2	Ugent_3	TUV_I	IFT_I[#]	SJAC
NO3	1.02	0.89	1.01	1.06	1.01	1.01	0.97	1.14
SO4	1.10	0.95	1.06	1.01	0.98	1.01	1.02	1.18

*Table 2.4 Ratio of the average concentration of nitrate and sulphate in PM2.5 over the campaign to the mean of all samplers, * without the 9th, # without the 11th*

PM2.5	IFT_LV	BTU_HV	IFT_HV[*]	Ugent_1	Ugent_2	Ugent_3	TUV_I	IFT_I[#]
NO3	1.03	0.90	0.88	0.97	1.04	0.98	1.07	0.94
SO4	1.04	1.14	1.03	0.97	0.93	0.88	1.04	0.92

standard deviation and 3.3 µg/m^3 with a 6 % relative standard deviation for PM10 and PM2.5, respectively. In Table 2.3 and 2.4 the relative ratios between the samplers are shown. All samplers are within 15 % of the average. Figure 2.2 compares the data for PM10 and PM2.5 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 PM10 and between 6 % and 30 % for PM2.5. The highest standard deviations are found for the lowest concentrations, as a result of a quite constant absolute difference of about 0.5 µg/m^3 between samplers (see Fig 2.3). Differences in the levels obtained with PM2.5 samplers were slightly higher, which may be explained by the different cut-offs used ranging from 2.0 to 3.5 µm. 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 (Acker et al., 2003) 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.

On average the SJAC data for PM10 seem to be slightly higher than the other data. Because the non-volatile sulphate shows the same feature (see Fig. 1b), we conclude that this finding can not be interpreted as a loss of nitrate by evaporation from the filters. Additionally, an absence of volatilisation is in good agreement with the comparability of the data from the inert and cellulose filters. The laboratory intercomparison showed that no volatilisation occurred from the latter, and we conclude that evaporation from the inert filters was not significant.

Ferm et al. (1988) compared different total nitrate samplers. For daily average total nitrate concentrations relative standard deviations were found to be lower than 15 % for different laboratories using the same sampling technique. At the low end of the concentration range (< 2 µg/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).
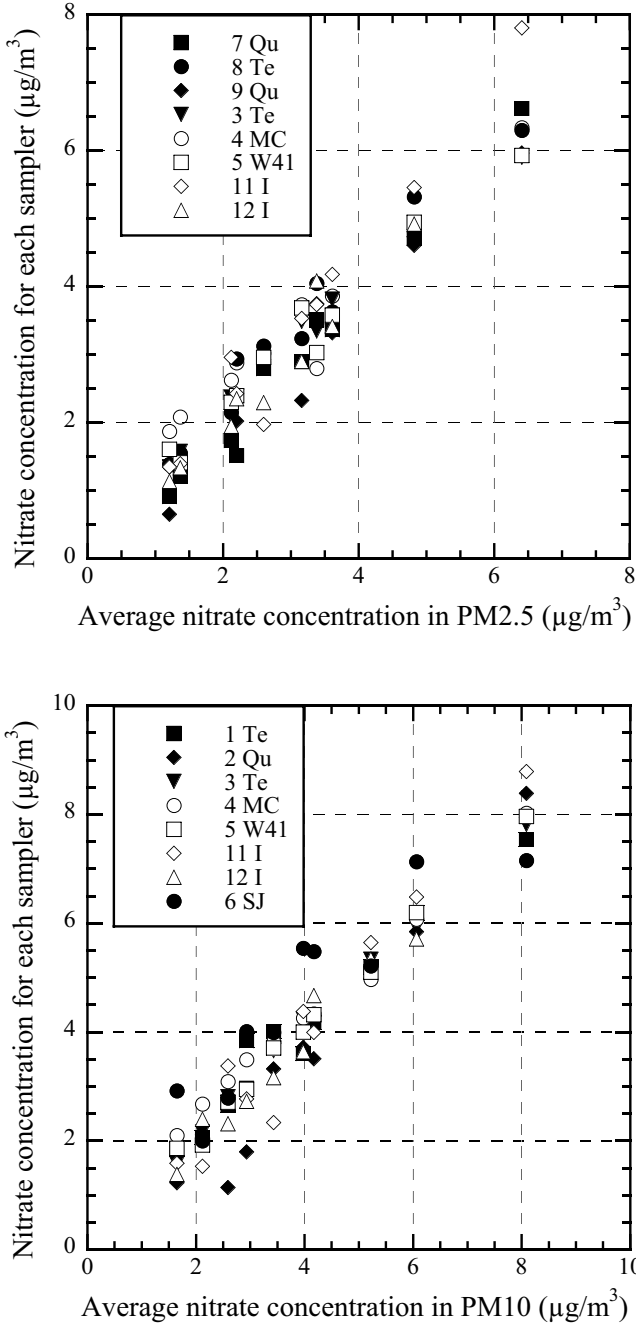
Figure 2.2 Comparison between the nitrate concentrations obtained from the individual samplers and the average nitrate concentration in PM2.5 (upper panel) and PM10 (lower panel). The numbers indicate the individual samplers (see Table 2.1) where the abbreviations denote its main feature: Te = Teflon, Qu = Quartz, MC = Mixed Cellulose ester, W41 = Whatman41, I = Impactor and SJ = SJAC.
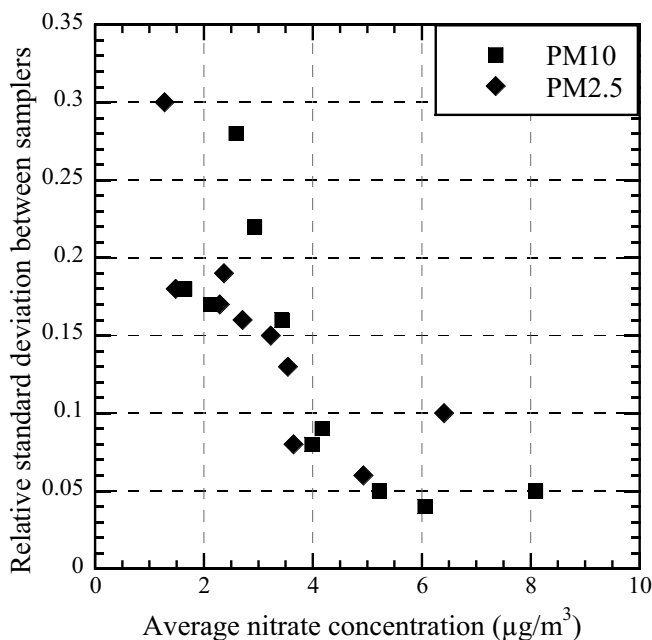
Figure 2.3 Relative standard deviation in the average of all samplers for PM2.5 and PM10 per day

2.3.2 Laboratory study

In the laboratory study the first step was to test the collection efficiency of the filters for sub-micron 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 24 °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 reference sampler. 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 μg/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 dis-equilibrium is indicated by the low concentrations of nitric acid, which were less than 10 % of the equilibrium value. In contrast to the inert-type 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 NH$_3$, which was present at a continuous background level.
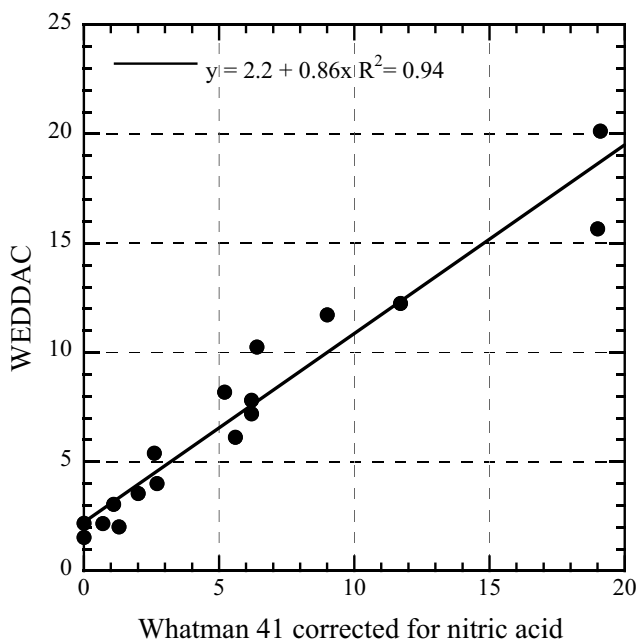
Figure 2.4 Concentration of nitrate as sampled on a Whatman 41 filter (corrected for HNO3) compared to the WEDDAC

Additional tests at a later date showed that on cellulose filters nitric acid is also retained 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.

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 2.2.

2.3.3   Po-Valley

During the late spring of 1998 an intercomparison of three samplers took place in the Po-Valley in a larger field campaign (PIPAPO). Some results of this campaign have already been reported (Putaud et al., 2002; Baltensperger et al., 2002). We provide here an evaluation of the nitrate concentrations as obtained with quartz filters, the Whatman 41 cellulose filters and the artefact free on-line method. Figure 2.4 compares the results of the cellulose filter measurements (Putaud et al., 2002) with those obtained by the WEDD/AC

Table 2.5 Po-Valley: ratio of nitrate on Quartz to Whatman41 filters, with and without correction for nitric acid absorption by the Whatman 41 filter.

Temperature (°C)	raw data	HNO3 corrected
< 20	0.58	0.93
20 – 25	0.29	0.41
> 25	0.07	0.08

system (Baltensperger et al., 2002). For this purpose, the measurements from the WEDD/AC system (20 minute resolution) were integrated for comparison with the longer sampling time of filters (4 - 7 hour resolution), correcting the filter data for the HNO$_3$ artefact (by subtracting the 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).

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 Figure 2.5 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 2.5 for these 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.

2.4 General discussion and implications for monitoring

2.4.1 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 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 experiment are (much) lower than the saturation limit.
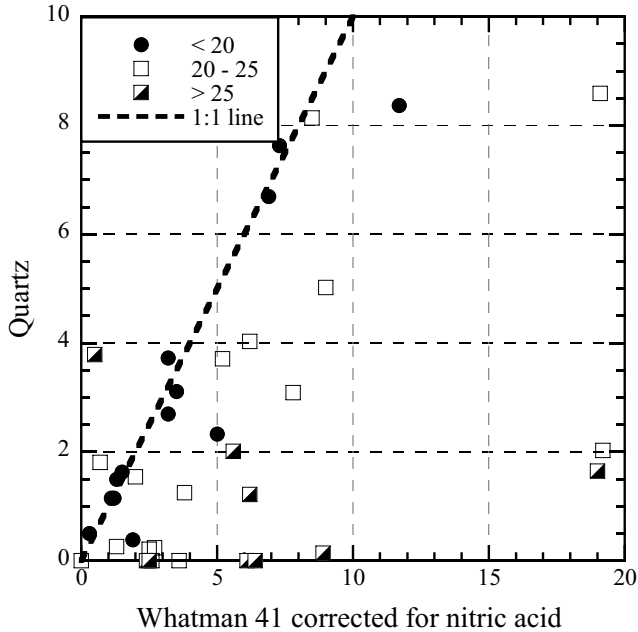
Figure 2.5 Concentration of nitrate as sampled on a quartz filter compared to that on a Whatman 41 filter (corrected for HNO₃)

2.4.2   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 Figure 2.5 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., 2003). At temperatures exceeding 25 °C during the Po Valley campaign and in the wind tunnel, complete loss of nitrate was observed, 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.

Losses during a 24-hour sampling period are 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 occur at the higher temperatures in the afternoon of the previous day but nitrate sampled at night 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.

2.5 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. 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 evaporation losses of aerosol-nitrate from the quartz filters used. We could parameterise the extend of the evaporation artefact as a function of temperature. There is complete evaporation at temperatures exceeding 25 °C and full retention at temperatures less than 20 °C. Between 20 and 25 °C the retention is on average 50 %, but with high variability.

A main conclusion from this study is that 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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