In situ speciation of trace Fe(II) and Fe(III) in atmospheric waters by the FZ method coupled to GFAAS analysis

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A quasi-on-line method of measurement of the oxidation states of iron coupled with a GFAAS analysis is reported for the trace conditions found in atmospheric waters. This technique is based on the formation of a specific complex $[Fe(FZ)_3]^{4-}$ between Fe(II) and ferrozine (FZ). tC_{18} solid-phase extraction cartridges (Sep-Pak) are used to separate the $[Fe(FZ)_3]^{4-}$ and Fe(III) so as to limit the risk of redox evolution of the sample. The adaptation to dilute aqueous media, via acidification at $pH = 2$ of rainwater sample, and atmospheric interferences are discussed, and the Fe(II) recovery in rainwaters is determined. This method coupled with a quasi-on-line sampling protocol has been tested on rains collected in Guadeloupe Island (Caribbean Sea, 16°N, 61°W) during a field campaign in May 2005. Our results show that the proposed method can satisfactorily be applied to the determination of Fe(II) and Fe(III) in atmospheric waters under *in situ* conditions.

Keywords: Iron oxidation state; Ferrozine method; Rainwater sampling; Atomic absorption spectrometry

1. Introduction

Extensive field measurements provide strong evidence that iron is the most abundant trace metal in atmospheric waters [1–4], where it occurs in particulate and dissolved forms, including both free and complexed ferrous and ferric iron species (denoted Fe(II) and Fe(III), respectively) [5, 6]. The concentration of dissolved iron species ranges from 10^{-8} to 10^{-4} mol L^{-1}, i.e. in the order of magnitude of hundreds of ppt to ppm [6, 7]. Dissolved iron participates in a variety of reactions including oxidation of S(IV) and organic compounds (e.g. formaldehyde, oxalic and pyruvic acids) by Fe(III) via direct electron transfer, and the catalytic autoxidation of S(IV) [8–11]. The oxidizing capacity of the troposphere is influenced by the reactivity and the redox speciation of Fe via its

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control on free radical production in clouds [12]. In addition to its role in the aqueous chemistry within the troposphere, Fe is also very important to the biogeochemistry of seawater. Indeed, phytoplankton growth and nitrogen fixation in the ocean are strongly influenced by Fe availability. Rain is a major source of iron to much of the open ocean [13]. The bioavailability of Fe is critically dependent on its redox speciation, since Fe(II) is more soluble than Fe(III) [6, 14, 15].

Measurements of iron oxidation states in cloud and fog water demonstrate that the ratio Fe(II) to total dissolved Fe can vary considerably between cloud or fog events (0.02–100%) with typical values superior to 50% [1, 4, 6, 16, 17]. The distribution of dissolved iron between the two oxidation states is a complex function of sunlight intensity, concentrations of oxidants (e.g. HO_2, O_2^-, H_2O_2, O_3, OH, O_2), reductants (e.g. Cu(I), S(IV)), and complexing agents (e.g. organic ligands). The existence of iron species in an aqueous solution is also a pronounced function of the pH [18]. Due to the combination of low concentrations and possible post-sampling evolution of oxidation states induced by the extreme reactivity of iron, direct measurement of Fe(II) in atmospheric waters, and generally in natural waters, is complicated. Thus, for studies into the redox speciation of Fe in natural waters, analytical techniques that minimize perturbations to the natural system are desired. Thereby, Das *et al.* [19] note that the determination of iron oxidation states in aqueous natural samples is conventionally achieved by the complexation with a specific chelating agent followed by spectrometric measurement [20–22].

Among the different chelating agents, PDTS, 3-(2-pyridyl)-5,6,-*bis*(4-phenylsulfonic acid)-1,2,4-triazine, commonly known as Ferrozine (FZ), has found wide use for the analysis of iron in natural waters since its introduction by Stookey [23]. FZ reacts with divalent Fe to form a stable magenta complex species $[Fe(FZ)_3]^{4-}$ with a maximum absorbance at 562 nm. Thus, Fe(II) is determined spectrometrically by adding FZ to the aqueous samples. At present, the ferrozine method coupled with long-pathlength liquid-waveguide-capillary-cell spectrometry is very sensitive and is usually used for iron speciation in atmospheric waters [24]. Nevertheless, this method implies the addition of FZ in the collected rainwater without separation of the redox forms of Fe, and hence a change in redox in Fe oxidation states is possible before or after FZ adding.

In order to limit the risk of evolution of iron speciation after sampling, it is important to separate both oxidation states of iron as soon as possible. To this purpose, the protocol using a pre-concentrated Fe(II) with Ferrozine adsorbed to tC18 Sep-Pak cartridges [25–27] seems to be the best suited. Samples were passed through the Sep-Pak with Fe(II) being retained as the coloured $[Fe(FZ)_3]^{4-}$ complex; Fe(III) was recuperated in the outflow of the cartridge; the complex was then eluted with methanol; and then the absorbance was measured by spectrophotometry. This method has usually been used for Fe(II) determination in seawater after *in situ* preconcentration [28]. This method is largely confirmed for studies of redox speciation of iron in seawater and freshwater, and the adaptation of this method to determine Fe(II) in atmospheric waters presents several difficulties. King *et al.* [25] emphasized that the decrease in FZ retention volume with decreasing mobile-phase ionic strength makes the method unsuitable for Fe(II) determination in dilute aqueous sample. They also demonstrated that the lower the ionic strength of the sample, the more the Fe(II) recovery will be reduced. The pH also plays an important role on the $[Fe(FZ)_3]^{4-}$ formation and hence on Fe(II) recovery. Thus, Gibbs [29] showed that a pH range of 3–6 could be relied on for a complete complexation, whereas the typical pH range for the atmospheric waters is 1–5.

King *et al.* [25] used a UV spectrometer to measure the $[Fe(FZ)_3]^{4-}$ in methanol. However, FZ, which is in excess, has a significant absorbance at the wavelength that is used for determination of complex, and hence can cause errors for samples with very low Fe(II) concentrations. In addition, it has been found that the FZ reagent usually contains trace amounts of impurities, which increase reagent blank absorbance [30]. A further adaptation of this method was made by Yi *et al.* [31], by analysing the eluted methanol using liquid chromatography (LC), which allowed the separation of the absorbance due to uncomplexed Ferrozine and impurities from the $[Fe(FZ)_3]^{4-}$ complex. This method increases the sensitivity of the analysis by removing interference that absorbs at similar wavelengths to the $[Fe(FZ)_3]^{4-}$ complex. The authors stated a detection limit of $0.1\,nmol\,L^{-1}$ for water. However, the LC using requires a step to evaporate methanol before analysis, which extends the protocol time.

This FZ method is well adapted to measure the Fe(II) content of wet aerosols or atmospheric waters due to its high sensitivity, high selectivity, and operational lightness in comparison with the other available techniques used for Fe(III) determination in atmospheric waters [5, 11, 16, 17, 21]. Compared with other highly sensitive methods using FZ, this quasi-on-line separation does not allow any change in iron redox state and enables the measurement of both Fe(II) and Fe(III). This is the reason why several studies have been carried out using the FZ method [6, 32–35] and particularly with the use of a pre-concentration step [4, 7, 31]. A graphite furnace atomic absorption spectrometer (GFAAS) is mostly used for trace-metal analysis in atmospheric samples due to its high sensitivity and lower limits of detection. Sofikitis *et al.* [36] have performed a method for iron analysis in the water–methanol matrix by GFAAS, which enables optimization of sensitivity and the sample time for the Fe(II) analysis. Based on both principles, this article describes the performance of on-line pre-concentration and the FZ method coupled with GFAAS for the determination of Fe(II) and Fe(III) in atmospheric waters.

2. Experimental

2.1 *Iron redox speciation method*

Fe(II) and Fe(III) were measured in filtered samples in duplicate using an adapted ferrozine spectrophotometry with a separation step on a Sep-Pack column. Ferrozine (FZ) is a complexing agent of Fe(II) which forms a magenta complex $[Fe(FZ)_3]^{4-}$. FZ loaded on a cartridge (Sep-Pak tC18) retained Fe(II) when a sample was passed through it, whereas Fe(III) was directly recovered at the outflow of the column. $[Fe(FZ)_3]^{4-}$ was eluted by methanol, and acidified MilliQ water was added with a methanol : water ratio of 20 : 80. Then, the Fe(II) concentration was obtained by measuring the Fe absorbance in the water–methanol Sep-Pak effluent by GFAAS. Fe(III) concentration corresponds to Fe measurement by GFAAS in the outflow sample of the Sep-Pak. To check the viability of the speciation measurement, total dissolved Fe was also measured in the initial sample with GFAAS. The analyses were performed according to the optimized protocol of Sofikitis *et al.* [36] for the water matrix and for water–methanol matrix. The Fe detection limits of GFAAS were $1.2\,nmol\,L^{-1}$ in water matrix and $3.6\,nmol\,L^{-1}$ in the water–methanol matrix, i.e. for Fe(III) and Fe(II) determination, respectively.

2.2 *Instrumentation*

An ATI-Unicam 929 GFAAS was used to analyse iron concentration. This GFAAS, especially designed for trace-metal analysis was installed in a clean laboratory and was equipped with Extended Life Cuvette (ELC) graphite tubes. The iron hollow-cathode lamp was operated at 20 mA with a slit corresponding to a spectral bandwidth of 0.2 nm and the 248.3-nm line monitored. The deuterium background correction was applied systematically.

2.3 *Reagents and cartridge*

All working solutions were stored in acid-cleaned PTFE bottles [37] at 4°C and were prepared in the ultra-clean laboratory (class <1000) or under ultra-clean laminar flow benches (class <10) with purified Milli-Q water. Sep-Pak cartridges packed with tC_{18} sorbents were obtained from Waters. These cartridges are silica-based bonded phases (trifunctional silicane bonding $-Si(C_{18}H_{37})_3$). FZ solution (6×10^{-3} M) was prepared from 0.62 g of commercially available purified FZ from Sigma dissolved in acidified Milli-Q (pH 2 by HNO_3 Normaton^{TM}). Methanol was ultra-pure solvent from J. T. Baker. Hydroxylamine ($1 g L^{-1}$) was prepared by dissolution of H_3NO, HCl (Fluka) in acidified Milli-Q. Fe(II) stock solution ($1.8 \mu mol L^{-1}$) was prepared by dissolving a $10^{-3} mol L^{-1}$ Fe(II) solution (0.392 g of ($FeSO_4$, $NH_4)_2SO_4 \cdot 6H_2O$) Normapur Prolabo^{TM} dissolved in 1 L of MilliQ water which was acidified by 10 mL of $10 mol L^{-1}$ H_2SO_4. The stock solution was diluted with MilliQ to freshly prepare the working solutions at the desired concentrations for experiments. Fe(III) working solutions were also prepared by dilution of a $18 \mu mol L^{-1}$ Fe(III) stock solution from $FeCl_3 \cdot 6 H_2O$.

2.4 *Loading and elution conditions*

Before first use, the Sep-Pak was washed by passing 10 mL of methanol, 10 mL of Milli-Q water, and 30 mL of pH 2 acidified Milli-Q water. Then, 10 mL of 6×10^{-3} M FZ solution was used to fix the Fe(II) impurity in the packing material, and 30 mL of a reducing agent, hydroxylamine, was added to reduce Fe(III) impurity. This procedure was performed three times over a 3-day period to reach a satisfactory decontamination level. Finally, the cartridge was eluted with 10 mL of methanol and then rinsed with 10 mL of Milli-Q water. The non-polar stationary phase of the column was then loaded by passing 15 mL of ferrozine 6×10^{-3} M. The cartridge was finally rinsed with 40 mL of acidified Milli-Q water to remove FZ in excess. In order to estimate the amount of FZ retained on the cartridge, five cartridges were loaded with FZ and rinsed with acidified waters to remove any non-adsorbed FZ. The retained FZ was then eluted and measured by colorimetry after Fe(II) addition. This experiment shows that, under our conditions, 19 μmol of FZ is retained on the cartridge.

The separation and elution scheme are shown in figure 1. Before passing through the cartridge, the samples were adjusted to pH 2 with HNO_3. Then, the samples were passed through the pre-prepared Sep-Pak cartridge at a rate of $10 mL min^{-1}$. By passing solution, Fe(II) was retained on the stationary phase in the form $[Fe(FZ)_3]^{4-}$ complex, while Fe(III) was directly recovered at the outflow of the cartridge. Since the

1. Water sample acidified pH=2
2. Methanol elution

FZ conditioned
tC18 cartridge

Fe(II) + 3 FZ → Fe(FZ)$_3^{2+}$

Peristaltic
pump

1. Fe(III) in water sample
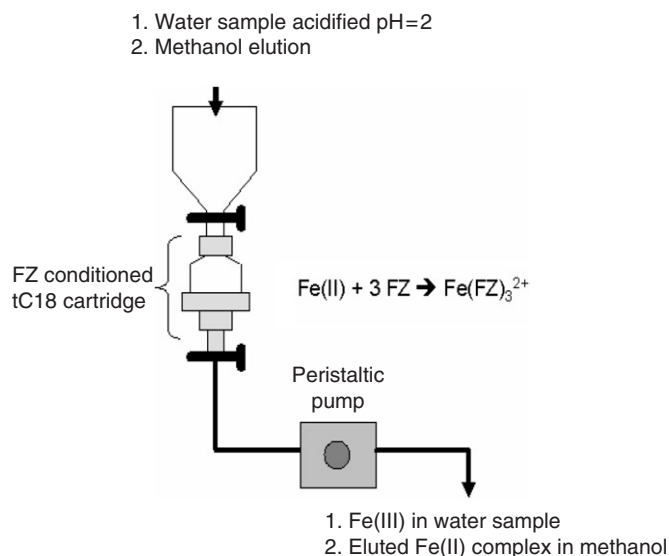2. Eluted Fe(II) complex in methanol

Figure 1.   Steps of iron speciation method by redox separation using a Sep-Pak cartridge preloaded with Ferrozine as a specific chelating agent of Fe(II).

complexation of one Fe(II) ion requires three molecules of ferrozine, the Sep-Pak is saturated for 6 µmol of Fe(II). This capacity was largely sufficient, even for the highest amount of iron found in the atmospheric samples. [Fe(FZ)$_3$]$^{4-}$ complex was then eluted with 6 mL of methanol. This organic fraction was completed to 30 mL with acidified water so that Fe(II) was finally in a water–FZ (80%) methanol (20%) mixed matrix. The separation protocol was completed in 3 min for 30 mL of sample from the sample introduction in the cartridge; the complete separation/elution procedure was finished in 10 min.

2.5 *Rainwaters*

The rainwater samples were collected from Feucherolles, a rural area close to Paris (France). As soon as a sample was collected in acid-cleaned bottles, it was filtered through a 0.2 µm Nuclepore acid-cleaned filter (1 h in 0.2 M HCl solution and then rinsed with MQ water) and acidified at pH 2 with nitric acid (Normaton^{TM}). Dissolved iron is defined as the fraction inferior to 0.2 µm which contains soluble iron (<0.03 µm) and colloidal iron (0.03–0.2 µm). The composition of rainwater has been determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis according to Desboeufs et al.'s protocol [37]. It appeared from these analyses that the chemical composition of this rainwater is in the usual range of rainwater composition [38, 39].

The synthetic rainwater was prepared by dissolution of 5 mg L^{-1} of Capo Verde loess (an analogue of Saharan aerosol), this solid/liquid ratio being typical of the rain loading charge [40]. In order to use this rainwater as a matrix to study the sample pH effect on the separation procedure, this synthetic rain was filtered after 15 min, and four aliquots were acidified with HNO$_3$ at pH 0.5, 1, 1.5, and 2, respectively.

Table 1. Number of micromoles of FZ retained by Sep-Pak as a function of pH and ionic strength of the mobile phase.

Retained FZ	
pH (μmol)	
1	19.0
2	19.3
3	3
4	1.8
Ionic strength (mol L^{-1})	
10^{-1}	17.5
10^{-2}	13.7
10^{-3}	2.2
10^{-4}	1.2

3. Results and discussion

3.1 *Adaptation of King's protocol to atmospheric waters*

King's protocol presents two problems to be adapted to atmospheric waters:

(1) King *et al.* [25] emphasize that the retention FZ on Sep-Pak packing material decreases with decreasing ionic strength of the mobile phase, and hence conclude that the method is unsuitable for Fe(II) determination in dilute aqueous samples. In the case of rainwater, the typical ionic strength is in the range of 0.02–3 mmol L^{-1} [41]. We tested the effect of ionic strength on FZ retention on Sep-Pak. A set of four FZ loaded cartridges were rinsed with NaCl solutions from 10^{-1} to 10^{-4} mol L^{-1} at pH 7 to study the ionic strength effect. The results (table 1) show that for the aqueous solutions with $I < 10^{-2}$ mol L^{-1}, the FZ retention clearly decreases.

(2) Gibbs [29] emphasizes that the $[Fe(FZ)_3]^{4-}$ complex is best formed in aqueous solution whose pH lies between 3 and 6 with a pH range depending on the buffer used. However, the typical pH range for the atmospheric waters is 1–5. The authors, working with the FZ method without a pre-concentration step, generally adjust the pH of their atmospheric samples around 4–6 with buffer to enable a complete complex formation [6, 30–35]. We have tested the pH effect on retention of FZ on the Sep-Pak with a set of four loaded cartridges which were rinsed with acidified solutions from pH 1 to 4 (table 1). The results show that for the aqueous solutions with pH > 2, the FZ retention clearly decreases, in part due to the decrease in ionic strength associated with pH increase. Thus, the strategy to buffer samples is not applicable with the use of tC$_{18}$, since we emphasized that the retention of FZ on the cartridge is also pH-dependent.

The three authors who already used the pre-concentration method for rainwater on Sep-Pak [4, 7, 31] have a different strategy to prevent these problems. In order to prevent the problem of FZ retention and Fe(II)/FZ complexation due to the low ionic strength of rain samples, Sedlak *et al.* [4] decided to add NaCl to the FZ solution and their samples prior to separation. For the same purpose, Yi *et al.* [31] and Zhuang *et al.* [7] preferred to acidify their samples at pH 2. We thought the choice of acidification would be more appropriate in our study, since this pH enables an ionic
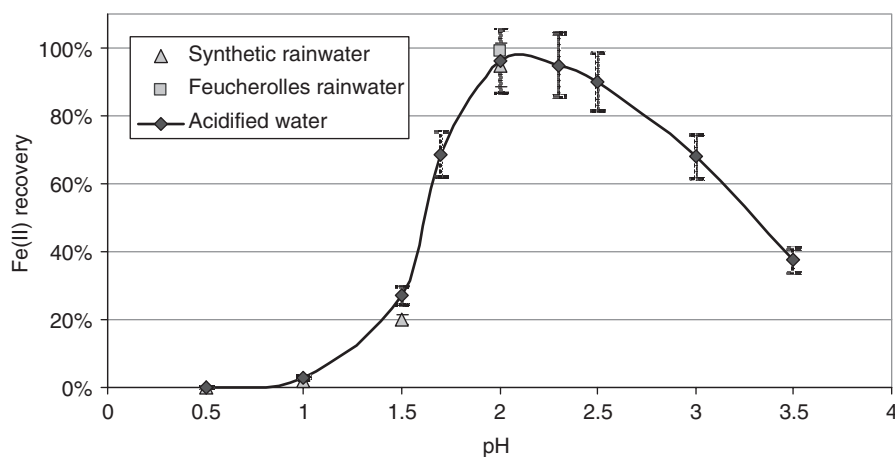
Figure 2.   Recovery efficiency of Fe(II) measured as a function of sample pH.

strength important enough to favour FZ retention. Furthermore, sample acidification is known to stablilize the Fe(II)/Fe(III) ratio in solution [32] and does not cause a complex matrix for analysis on the contrary of NaCl addition. However, this pH is not in keeping with the results obtained by Gibbs in the pH range 3–6 where the $[Fe(FZ)_3]^{4-}$ complex is completely formed. The recovery efficiency of Fe(II) on Sep-Pak was carried out by adding a known amount of Fe(II) standard on acidified MilliQ solutions for a pH range of 0.5–3.5. The recovery of Fe(II) is dependent on pH (figure 2) with an optimal Fe(II) recovery superior to 95% between pH 2 and 2.3. This Fe(II) recovery is in good agreement with the values of 92–99% found by Yi *et al.* [31] with an acidification to pH 2. When the pH is less than 2, a sufficient $[Fe(FZ)_3]^{4-}$ complex formation is not achieved to enable a good recovery efficiency. When the pH is higher than 2.3, the ionic strength is too low to enable good FZ retention on Sep-Pak, as observed in figure 2. Thus, the range of work is limited, and we chose to use acidification of samples to pH 2. In order to confirm the results obtained with the acidified water, and particularly the efficiency of complex formation even in a rain matrix, recovery of Fe(II) from the Sep-Pak cartridge was also determined by the addition of known amounts of Fe(II) standard to aged Feucherolles rainwater samples acidified at pH 2 and for synthetic rainwater acidified at pH 0.5, 1, 1.5, and 2. The results (figure 2) show that the Fe(II) recovery found with rainwater samples is similar to that for acidified water and hence confirms the reliability of the speciation method with acidification at pH 2.

The step of acidification at pH 2 of the sample implies that the pre-concentration on the Sep-Pak cartridge cannot be carried out on-line for rain sampling. Classically, the acidification is made as soon as the sample is collected. So, we have measured the ratio of Fe(II)/Fe$_{total}$ in a dilute HNO$_3$ solution to pH 4.5 for 10 min. The decision to work with a simple nitric acid solution, rather than with rainwater, is based on the results of Kieber *et al.* [42]: the Fe(II) concentrations in six rainwater samples and in a dilute H$_2$SO$_4$ solution spiked with inorganic Fe(II) were measured initially and after 24 h of storage in the dark at room temperature. There was no statistical difference for Fe(II) concentrations for the six rainwater despite their compositional variations, but the Fe(II) in the dilute acid solutions decreased by more than 80% in both samples

after 24 h. Kieber *et al.* [42] conclude that Fe ligands present in rainwater stabilize Fe(II) against oxidation. Thus, the Fe(II) evolution will be optimal in a simple acid solution. Our results show that even in this worst condition, during a 10-min period, no significant redox change has been observed for a dilute HNO_3 solution to pH 4.5, a typical pH of rainwater. This result is also in agreement with Majestic *et al.*'s experiments [24] testing the stability of iron oxidation states in samples stored at pH 4.3 in acetate buffer over 24 h. An analogous experiment was performed with a HNO_3 solution at pH 2 for 1 h to determine the stability of samples after acidification. An acidified solution (HNO_3, pH 2) has been prepared with an initial Fe(II)/Fe$_{tot}$ ratio of 80% and stored at room temperature. The Fe(II) and Fe(III) measurements show that no significant change in redox ratio occurs over 1 h, even without storage in the dark.

Fe(III) can react with FZ, thereby interfering with Fe(II) determination [43]. Moreover, the reduction of Fe(III) during the analysis could introduce an artefact on the Fe(II) determination. As a consequence, probable analytical effects of Fe(III) on Fe(II) determination during analysis were investigated. First, Fe(III) solutions at various concentrations (in dilute HNO_3 solution to 0, 36, 90, and 180 nmol L^{-1}) were passed through the loaded Sep-Pak. There was no detectable Fe in the methanol/water eluent, indicating that there was no retention and no reduction of Fe(III) by FZ (table 2). Second, the Fe(II) recovery was determined for solutions with a known Fe(II)/Fe(III) ratio. It appears that there was no detectable interference on Fe(II) determination, irrespective of the Fe(II)/Fe(III) ratio (table 2).

3.2 *Fe(II) recovery in atmospheric waters*

The proposed analytical strategy was applied to direct determination of iron redox speciation of rainwater (Feucherolles rainwater). The recovery of Fe(II) from the Sep-Pak was determined by spiking a rainwater sample with 150 nmol L^{-1} Fe(II). The recovered Fe(II) concentration is the measured Fe(II) in the water–methanol Sep-Pak effluent minus the Fe(II) concentration in the rain samples, measured beforehand. The recovery of Fe(II) was around 99% (table 3), indicating the validity of

Table 2. Effect of Fe(III) on Fe(II) retention: concentrations (nmol L^{-1}) before (pre-) and after (post-) separation on Sep-Pak Cartridges.

Experiment no.	Pre-Fe(II)	Measured post Fe(II)	$\pm$SD	Pre-Fe(III)	Measured post-Fe(III)	$\pm$SD
	0	< DL[a]		0	< DL	
	0	< DL		236	382.1	20.08
1	0	< DL		905	884.9	40.18
	0	< DL		1800	1769.8	60.33
	590	884.9	40.11	0	< DL	
2	905	915.1	40.21	236	382.1	20.06
	905	975.4	60.32	590	844.7	40.14
	905	955.3	60.3	10,180	1639.1	60.25
	0	< DL		905	884.9	40.14
3	236	1.934	0.208	905	884.9	40.13
	905	915.1	40.2	905	864.8	40.13
	18010	18010	110.6	905	915.1	40.17

[a]DL = detection limit.

this method to atmospheric waters. The precision on these measurements was 5%. Moreover, the recovery is in the same order of magnitude of the recovery in MilliQ water matrix at pH 2 (figure 2), proving that the Fe(II) recovery is not affected by the other compounds present in rainwater. Blanks were obtained by passing 30 mL of acidified water (pH 2) through the loaded cartridge. The Fe(III) blank corresponded to acidified water recuperated in the outflow of the cartridge, and the Fe(II) blank was obtained by eluting the same cartridge with 6 mL of methanol. In these conditions, the detection limit is about $3.6\,\mathrm{nmol\,L^{-1}}$ for Fe(III) and $5.4\,\mathrm{nmol\,L^{-1}}$ for Fe(II), taken as three times the standard deviation of 10 acidified reagent blanks, respectively, in the outflow and in the water–methanol effluent from the Sep-Pak.

Rainwater was also analysed by ICP-AES before and after being passed through the cartridge to observe which compounds can be retained or contaminated by the cartridge. A strong contamination in Si and S appeared ($+3000\%$ and $+1000\%$), the Si contamination was probably related to the nature of Sep-Pak cartridge (which is a silica-based bonded phase), and the S contamination may come from FZ itself which contains the $-SO_3$ functional group. We noticed also that Cu was retained by the cartridge. It is know that FZ can form a complex with Cu(I), indicating a possible application of this method to study Cu speciation in rainwaters. Although Cu(I) has no effect on the recovery of Fe(II), the opposite effect must be checked before such an analysis can be applied.

3.3 In situ *rainwater sampling and analysis*

Due to the constraints imposed by the acidification step at pH 2, it is impossible to carry out an on-line separation. However, in order to limit the risk of change in the iron redox state of the rain sample, we developed a procedure in which the separation between Fe(II) and Fe(III) is quasi-on-line. The rainwater samples were collected with a pre-cleaned collector system consisting of a PTFE funnel tooled up with an on-line filtration system ($0.2\,\mu\mathrm{m}$ Nuclepore) screwed into a pre-acidified polyethylene bottle. Each pre-acidified bottle contained an amount of nitric acid necessary to adjust the pH to 2 for a rain volume of 30 mL. The acidification step enables the ratio Fe(II)/Fe(III) in solution to be stabilized, and the on-line filtration prevents dissolution of the aerosol in acid environments and hence the increase in dissolved Fe concentration. This pre-acidification step requires a rain volume of at least 30 mL. If the collecting volume is more than 30 mL, the pH needs to be adjusted at 2 afterwards by addition of nitric acid. Three millilitres of the sample are kept for total iron measurement by GFSAA.

Table 3.   Recovery efficiency of Fe(II) in rainwater collected in Feucherolles.

	Rainwater Fe total concentration $(\mathrm{nmol\,L^{-1}})$	Rainwater Fe(II) concentration $(\mathrm{nmol\,L^{-1}})$ (1)	Added Fe(II) concentration $(\mathrm{nmol\,L^{-1}})$	Total measured Fe(II) concentration $(\mathrm{nmol\,L^{-1}})$ (2)	Recovery Fe(II) concentration $(\mathrm{nmol\,L^{-1}})$ (2)–(1)	Recovery (%)
Rainwater	45	39	149	188	149	100
Rainwater +hydroxylamine	45	45	147	192	145	99

[a](1): natural Fe(II) concentration in rainwater. (2) Fe(II) concentration in rainwater after adding of Fe(II). (2)–(1): total measured Fe(II) concentration minus Fe(II) concentration present in natural rainwater.
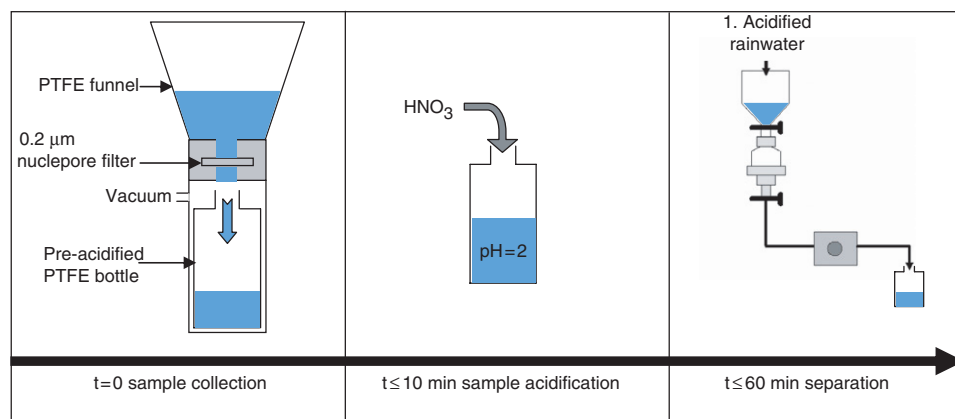
Figure 3. Description of the rainwater sampling and analysis: (1) sampling and on-line filtration of rainwater with pre-acidification; (2) adjustment of pH 2 with nitric acid; (3) separation of filtered and acidified rainwater.

Table 4. Guadeloupe rainwater measurements ($nmol\,L^{-1}$).

Date	Volume (mL)	$Fe_{tot,dis}$	$Fe(III)_{dis}$	$Fe(II)_{dis}$
8 May	27	220 ± 4	18.1 ± 0.9	194 ± 18
10 May	44	96 ± 2	5.0 ± 0.3	93 ± 9
10 May	15	24 ± 1	$< DL$	23 ± 3
11 May	55	92 ± 2	26 ± 2	64 ± 6

The cartridge loaded with Fe(II) is then stocked and eluted at the laboratory. Tests showed that the cartridge elution can be performed until 5 days after the sampling.

Four rainwater events were collected in Guadeloupe Island (Caribbean Sea, 16°N, 61°W) in May 2005. The proposed sampling and analytical strategy (figure 3) was applied to determine iron redox speciation in Guadeloupe rainwater. The total dissolved Fe, Fe(II), and Fe(III) concentrations in rain samples collected in May 2005 are shown in table 4. Although the total dissolved iron varies greatly from one sample to another (between 24 ± 2 and $212 \pm 2\,nmol\,L^{-1}$), the Fe(II) concentration represents a significant fraction of the total filtered Fe in any sample. Fe(II) contributes to 70–97% of the total dissolved Fe. The total dissolved concentrations of any samples are similar to values obtained by Kieber *et al.* in Bermuda, whereas the contributions of Fe(II) on the total dissolved iron are greater in this work (table 4).

4. Conclusion

No interference due to the presence of other ions that might form complexes with FZ has been detected. We have checked that the FZ/Sep-Pak method coupled with GFAAS analysis enables a good Fe(II) recovery . In atmospheric waters, the Fe concentrations are 10^{-8} to $10^{-4}\,mol\,L^{-1}$. The method is characterized by detection limits of $5.4 \times 10^{-9}\,mol\,L^{-1}$ for Fe(II) and $3.6 \times 10^{-9}\,mol\,L^{-1}$ for Fe(III) with a sampling

volume of 30 mL, corresponding to the volumes and concentrations of rainwater during field collections. Thus, these results demonstrate that this method is well suited to Fe(II) determination in atmospheric waters. The results also emphasize a possible application of this method for Cu speciation.

Acknowledgements

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