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# Behavior and Determination of Titanium Dioxide Nanoparticles in Nitric Acid and River Water by ICP Spectrometry

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S *Supporting Information*

ABSTRACT: ICP spectrometry (ICPMS, ICPOES) are classical techniques for the determination of solubilized or suspended elements. Unfortunately, their relevance for nanoparticles at low concentration (below 10 ppm) is rarely called into question, even if literature reports are not always coherent. This work is a systematic study based on the measurement of TiO_2 nanoparticle suspensions, as a model of quasi-insoluble material, by plasma spectrometry. It studies both sample treatment and measurement in the 10 ppb to 30 ppm concentration range. Realized on a set of four engineered nanoparticles suspensions at low concentration, it shows the existence of three different regimes of stability that affect concentration measurement. Above a C^S stability concentration value, suspensions are stable in time; below a low-concentration C^E value, the signal loss is at a maximum, and a final partition is reached between the container walls and the suspension. Between these two regimes, the suspension aging varies with concentration. C^E and C^S depend on nanoparticle characteristics and the suspension medium, whereas the evolution kinetic is volume-dependent. Because TiO_2 nanoparticles are present in the environment at concentration below C^S, it is then necessary to find a way to rehomogenize the suspension between sampling and analyzing. Soft sonication, minimizing the sample temperature, and trapping of free radicals is proposed and evaluated. Homogenization is traced by the addition of an internal standard before storage. The procedure is applied to a real sample, Seine River water. The amount of total titanium found, 48.7 ppb, is in good agreement with the result of the reference method.
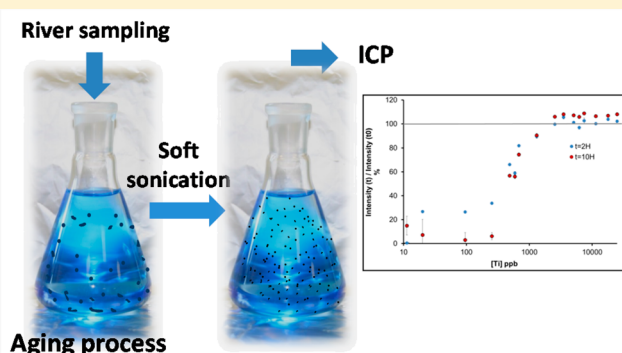
The last two decades have witnessed the emergence of a very large variety of engineered nanomaterials. Among those carrying the great expectations of nanotechnologies, some are new versions of materials already having dedicated applications, and others are more innovative and in a stage where massive applications are not yet in place. Oxide nanoparticles (e.g., SiO_2, TiO_2, CeO_2) are among the first group. They were essentially chosen because of the enhanced reactivity due to their small size.[1] They show applications in various fields, such as food and tire reinforcement for SiO_2, soot degradation for CeO_2, skin solar protection,[2] and building photo catalytic coatings for TiO_2.

Their potential impact on the living world,[3] their dissemination,[4] and the ultimate fate in the environment[5] has become a social concern, although whatever transport medium and assumptions in modelization, the anticipated concentrations are relatively low[6] (in the range of a few parts per billion). Because the engineered nanomaterials are designed to exhibit important chemical activities compared with larger particles, there is, despite these low concentrations, a need for risk analysis, which requires ecotoxicity studies and quantitative determination of exposure concentrations in the environment. This work provides a means to achieve this last point. Focused on TiO_2 nanoparticles as a model of quasi-insoluble materials, it describes the required controls and the resulting implications for accurate determinations.

Inductively coupled plasma spectrometers (ICPOES and ICPMS) are widely used for quantitative element determination in solution but also increasingly for that in suspension.[6−8] ICP spectrometers can be used alone for direct quantification of suspended nanoparticles, as in the single particle mode,[9] but also as separation technique detectors (LC−ICPMS, FFF−ICPMS,[2,10] etc.).

Quantitative determination of suspended TiO_2 nanoparticles has already been broached by plasma spectrometry. In 2004, the determination of impurities in ground Standard Reference Materials (SRM) grade TiO_2 powder (0−15 μm) and homemade nanometer particles (0−100 nm) in suspension

was compared with certified values (for the SRM sample), acid digestion, and alkaline fusion results.[11] A dispersant was required because preparation in aqueous solution alone appeared unsuitable owing to agglomeration or flocculation effects. The addition of dispersant or surfactant is a widespread method for the stabilization of synthetic liquid suspensions.[8] It is particularly well suited for the determination of particle impurities, only elemental ratios being measured.[12] The choice of a dispersant implies good knowledge of the suspension composition (particle bulk composition, amounts) because an excess could be detrimental to the stabilization.[8] In 2006, B. Hu et al. compared the performances of slurry nebulization and electrothermal vaporization for the determination of impurities in the liquid suspensions of three TiO_2 powders using a surfactant and sonication.[13] Also in 2006, the determination of the amount of low-concentration (100 ppt) manufactured 20-nm-diameter TiO_2 nanoparticles was obtained by an in-torch vaporization device installed on a high-resolution ICPMS.[14]

These publications as well as the recent article of D. Lison[15] et al. on determination of SiO_2 nanoparticles highlight the importance of sample preparation, which is inseparable from the measurement itself. The variety and the empirical character of experimental approaches generally hinder direct comparison of results obtained from different studies. There is thus a need for more systematic analytical studies including not only the measurement itself but also sample preparation to produce meaningful data. In this context, the first part of this work is dedicated to the ICPOES titanium direct measurement of synthetic suspensions prepared from a set of four engineered commercial TiO_2 nanoparticles. The nanoparticles were chosen for their size and stabilization treatment diversitiy, and the suspensions were studied through time under a large range of concentrations (30 ppm to 10 ppb). A systematic sample preparation study highlights parameters of importance. It is a prerequisite work to better understand the sample aging process that degrades suspension homogeneity. It provides a path to circumvent any influencing parameters that may have a disastrous effect on measurements. From this study, a new specific sample treatment of suspensions is proposed for ICP measurements. Based mainly on soft sonication and internal standard addition, this procedure is validated by ICPMS on river water real samples.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Five TiO_2 (nano)particle commercial samples have been investigated (Table 1). Specpure Titanium IV oxide with certified composition was used for optimization and validation of a fusion dissolution procedure. Three nanoparticle suspensions here were purely anatase (Ana-120, Ana-101, Ana-102), and the last one was purely rutile (Ru-104). The Ana-120 was purchased as stable liquid suspension in pH 1.5 medium, the three other nanomaterials were sourced as powders. Ru-104 was suspected to be coated with Al_2O_3 and with an organic modifier to exhibit hydrophilic properties.[16]

Standard titanium solutions were prepared by weight dilution in pH 1.5 HNO_3 of standard 10 000 mg/L Ti (Spex-CertiPrep, Metuchen, USA). Sodium dihydrogen phosphate monohydrate $NaH_2PO_4 \cdot H_2O$ (Sigma chemicals) and disodium hydrogen phosphate Na_2HPO_4 (Prolabo, Paris, France) were of ACS and Normapur grade, respectively. Nitric solutions are prepared by dilution of HNO_3 to pH 1.5 (Suprapur, Merck). Co was purchased as 10 000 mg/L in HNO_3 (Spex-Certiprep), HCl

Table 1. TiO_2 Nanoparticles and Particles Studied[a]

sample	product information	composition	crystallite size (nm)	purity (%)	BET surface area (m²/g)	Z_{avg} (nm), Pdl; Z (nm) (% vol) t = 0 h	Z_{avg} (nm), Pdl; Z (nm) (% vol) t = 24 h	ζ_{avg} (mV)
Ana-120	Nanostructure and Amorphous Materials Inc., Houston, Texas	anatase dispersion in water 15%(w) TiO_2	5–30 nm	99.5		34 (0.239), 22 (99.6%), 46 (0.4%)	35 (0.254), 21 (99.4%), 4651 (0.3%)	0.3
Ana-101	Hombikat UV-100 Sachtleben	Anatase powder	<10 nm	91	>250	615 (0.368), 165 (2%), 1087 (51%), 5396 (47%)	673 (0.342), 860 (22%), 5301 (78%)	30
Ana-102	PC105 Crystal Global	anatase powder		95	90	770 (0.427), 1068 (34%), 5376 (65%), 187 (2%)	998 (0.324), 1027 (33%), 5457 (67%)	35
Ru-104	UV-Titan M212 Sachtleben	rutile powder; hydrophilic coating: Al_2O_3 6%, glycerin 1%	20 nm	90	60	190.8 (0.227), 139 (50%), 4875 (50%)	178 (0.208), 134 (54%), 46 (46%)	36
SPec	Johnson Mattey Chemicals, Royston, UK	Specpure Ti IV oxide powder		>99.9				

[a]Composition, crystallite size, purity, and surface area were provided by the suppliers. Volume size distributions with polydispersity indexes (Pdl) and ζ potentials were measured by DLS at different suspension ages in pH 1.5 HNO_3 [Ti] = 30 ppm.

was of analytical grade (Merck), and isopropyl alcohol was from Sigma Aldrich. Seine River water used for the preparation of commercial nanoparticles suspension in river water medium was sampled in Paris near the Tolbiac bridge and filtered on a 0.22 μm filter before use.

Vials, jars, and Erlenmeyers were cleaned according to the procedure proposed in the Supporting Information (SI1).

Sonication was performed in a bath (Elmasonic P30H model). The samples were regularly moved in the bath for a better homogeneity of sonication.

Dynamic Light Scattering. Nanoparticle size distribution and ζ-potentials were measured on TiO_2 suspensions by Dynamic Light Scattering (DLS, Nano Zetasizer, Malvern Instruments). The suspensions were not sonicated prior to measurement, but they were filtered (1 mm, cellulose) to eliminate dust. Size results are reported as volume distribution. This is most consistent for an ICP spectrometer determination, as opposed to intensity or number distribution. The volume distribution implicitly assumes spherical nanoparticles.

ICPOES and ICPMS Analysis. All concentrations refer to the amount of titanium (parts per billion) whether it is TiO_2 nanoparticles suspensions or Ti in solution.

Titanium determination was performed by ICP OES (Optima 2000DV, Perkin-Elmer, Uberlingen, Germany) on an apparatus equipped with a slurry nebulizer (Glass Expansion, Melbourne, Australia) and a glass cyclonic chamber. For direct determinations of nanoparticle suspensions, a multiposition, motorless magnetic stirrer (Variomag, ThermoScientific) was placed on the autosampler to agitate sample volumes up to 1 L. This setup ensures controlled and identical operating conditions for all the vials (identical vials, identical sample levels in vials but also identical autosampler probe aspiration positions in the suspension, identical stirring bars and speed, etc.). Two emission wavelengths were selected for the titanium measurements: 334.950 nm for concentrations lower than 10 ppm and 323.657 nm for those between 10 and 100 ppm.

Titanium determination was also performed by quadrupole ICPMS (X series, Thermo Elemental). The instrument was equipped with a slurry nebulizer and an impact ball nebulization chamber. Titanium was measured on masses of 47, 49, and 50. Mass 50 was used for quantitative determination in the river water. [59]Co present at a very low level in the Seine River[17] was used when noted as the internal standard. For Seine River measurements, blank river water samples were obtained by filtration of river water on a 0.22 μm filter after acidification by nitric acid or aqua regia. The amount of titanium in solution in the Seine River measured elsewhere[17] reached 60± 10 ppt, which was too low to be measured by the instrument. The signal observed on the blank river water sample at the mass 50 was due to the interference [13]C[37]Cl. Blank samples were also used to prepare engineered commercial nanoparticle suspensions in river water medium.

Repeatability was calculated for both ICPOES and ICPMS as the relative standard deviation (RSD) on six consecutive replicates of the same sample. Interval reproducibility was evaluated on several suspensions of the same age. Age reproducibility was calculated by measuring the same sample at different times.

Fusion Dissolution. Titanium dioxide dissolution performed here consisted of an adaptation of the dissolution procedure proposed by Radhamani.[18] A polyphosphate flux was first prepared in a dry platinum crucible by mixing 3 g of sodium dihydrogen phosphate monohydrate with 3 g of

disodium hydrogen phosphate. The mix was heated in an oven at 850 °C for 2 h before rapid cooling. The condensed phosphate formed was then removed and transferred to a second dry platinum crucible. This second crucible was then covered with a platinum lid and heated to 1000 °C for 45 min. After cooling, the melt was dissolved in hot water. The sample obtained was diluted in nitric acid and analyzed by ICPOES by standard addition. The method was validated on Spec TiO_2 particles 99.95% purity and on each engineered nanoparticle studied. When TiO_2 nanoparticles were purchased as water dispersion, the suspension was first dried at 80 °C in an oven. For river water, large volumes (>1 L) were sampled and transferred into PFA bottles in the laboratory, where they were rapidly filtered on 0.22 μm cellulose. Filters were calcinated in the oven. The fusion was then performed as described above.

■ RESULTS AND DISCUSSION

Nanoparticle Suspension Characterization. The four engineered commercial nanoparticles (Ana-120, Ru-104, Ana-101 and Ana-102) were characterized in suspensions by DLS. These experiments were realized at very high concentrations (30 ppm in Ti or 50 ppm in TiO_2) because of the low sensitivity of the technique. Suspensions were prepared in pH 1.5 nitric acid medium to impose a pH far from the isoelectric points (pH 6−8) of the TiO_2 nanoparticles. The surface of the TiO_2 nanoparticles was positively charged, and the suspension stabilization was favored.[16] The different ζ potentials are shown in Table 1. They range between +30 and +36 mV for all the nanoparticles, highlighting the suspensions' stabilities, except for the Ana-120, which is neutral at the pH value chosen. This difference is very probably due to the presence of a dispersant in the Ana-120 commercial suspension covering the nanoparticle surface and ensuring the dispersion.

DLS volume distributions are also shown at different suspensions ages (0, 2, and 24 h) in Table 1 and in the Supporting Information (Figure S1). Ana-120 shows very low aggregation, with an average aggregate diameter of 25 nm, the suspension having been stable for 24 h. When suspended (t = 0), Ru-104 showed two aggregate populations centered on 150 nm and a few micrometers, respectively. The huge aggregates were present in the same proportion after 2 h, but clearly formed a deposit after 24 h, allowing a population of very small aggregates centered at 46 nm in diameter to appear. Both Ana-102 and Ana-101 show two aggregate populations centered around 700 and 5000 nm in diameter. These distributions evolved little with time.

Suspension Behavior in pH 1.5 Nitric Acid Medium. The first concentration measurements were carried out with an ICPOES on suspensions containing one or the other of the nanoparticles at various concentrations (10 ppb to 30 ppm) and ages (5 min to several hours). Whichever the nanoparticles tested, preliminary results showed poor reproducibility, especially at low concentration. They also showed uncontrolled and irregular evolution with age. More precisely, ICP signal intensities decreased with suspension age in most of the suspensions studied. Table 2 gives an illustration of the phenomenon with Ru-104. A suspension was distributed over several identical vials, and the titanium signal was measured in each vial just after preparation and 3 h later. In this example, signal repeatabilities and interval reproducibilities were in the range of ICP performances. However, during the 3 h of aging, the average Ti signal intensity decreased by 37%. It should be pointed out that these observations seem to be in contradiction

Table 2. Influence of Sonication and Aging on Signal Repeatability and Reproducibility[a]

suspension age	average signal (cps)	repeatability RSD (%)	interval reproducibility RSD (%)
Without Sonication			
<5 min	$7 \times 10^{+5}$	<4	1.6
3 h	$4.3 \times 10^{+5}$	<4	2.1
After Sonication (5 min for each PFA jar)			
<5 min (after sonication)	$7.4 \times 10^{+5}$	<4	7.4
25 min (after sonication)	$6.2 \times 10^{+5}$	<3	14.9
45 min (after sonication)	$5 \times 10^{+5}$	<3	27.8

[a]Conditions: Ru-104 in HNO_3 pH 1.5, [Ti] = 470 ppb, magnetic stirring, 5 identical 60 mL PFA jars.

with the previous DLS measurements, showing that Ru-104 suspension is stable for at least 2 h. This behavior was also observed with the other nanoparticles, as, for example, with Ana-120, the suspensions of which seem to be stable by DLS for 24 h. This apparent contradiction should nevertheless be tempered. Numerous parameters influencing suspensions (volumes, temperature, concentration, etc.) vary among characterization techniques. Moreover, the two techniques do not sample the suspension in the same way and are thus differently sensitive to its heterogeneity.

To find the relevant parameters and to be able to predict the behavior of the suspensions, a systematic study was undertaken. It focused on ICPOES measurements of Ru-104 in suspension at low level concentration.

Influence of Container on Signal Intensity at Constant Ru-104 Nanoparticles Concentration. A large-volume suspension was prepared and poured into PFA and polypropylene containers and measured at regular time intervals. The vials were selected in such a way that for the same volume, all the vials, whatever their material, have exactly the same shape. PFA vials were chosen for their great variety of shape and size, reusability, low adsorption and washout properties. Polypropylene was selected for its disposable nature. Results are shown in Figure 1. For all the containers tested, ICP signal intensities decreased when suspensions aged. This intensity diminution is related to the container volume but not to its material composition. It also seems that the surface condition has no impact on the suspension evolution. Pristine, brand-new, and several times-reused scratched PFA-surface
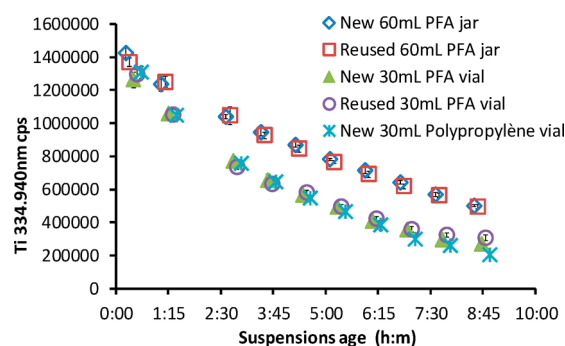
Figure 1. Signal intensity evolution with time of a suspension of Ru-104 at 1000 ppb in nitric acid pH 1.5 under magnetic stirring for different containers.

vials show exactly the same results; thus, the only influencing parameters here are the suspension volume and age.

To go further into detail, a new suspension of Ru-104 was prepared and divided into PFA jars of different volumes (7 to 1000 mL) and analyzed through time under constant magnetic stirring to minimize possible sedimentation. (Figure 2). Signal
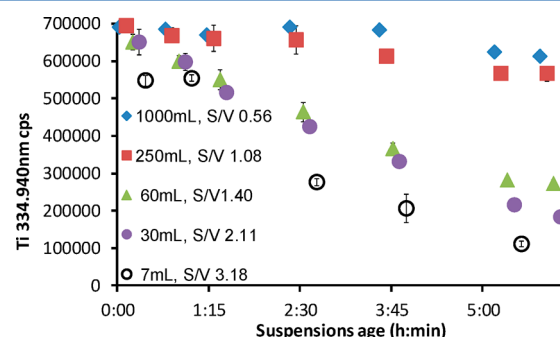
Figure 2. Signal intensity evolution with time of a suspension of Ru-104 at 730 ppb in nitric acid pH 1.5 under magnetic stirring for different PFA containers. The 7 mL experiment is realized with five vials. S/V: surface to volume ratio.

loss is clearly related to the vial volume or, more certainly, to the surface-to-volume ratio. Large-volume suspensions could be stable for 2 h, whereas 60 mL or smaller sample should be analyzed as soon as possible. Nevertheless, this observation has to be further refined: suspension volumes change during analysis because of sample consumption, amplifying the smallest containers' lack of reproducibility.

Influence of Ru-104 Nanoparticles' Concentration at Constant Vial Volume. In this set of experiments, the sample volume was kept constant as far as possible, despite the samples' uptake. To achieve this, several experimental dispositions were taken (Supporting Information SI2, Figure 3). The (I_{2h}/I_0) variation curve appears surprisingly as two
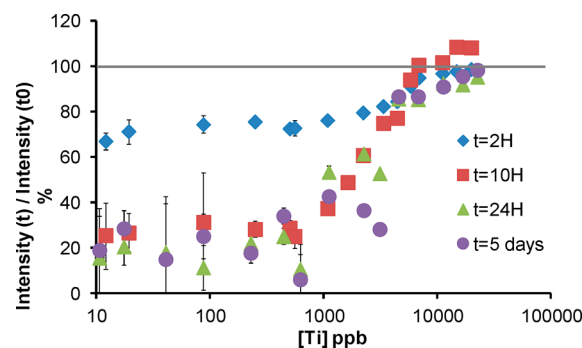
Figure 3. Influence of Ru-104 suspension concentration on signal measured at several ages (t). The reference (100%) is measured at $t <$ 5 min. Suspension: Ru-104 in nitric acid pH 1.5 under magnetic stirring in 60 mL PFA jars.

plateau zones joined by a sharp slope region. The most concentrated TiO_2 suspensions ([Ti] > 7 ppm) showed little evolution with aging. In the next decade range (0.5−7 ppm), the ICPOES signal intensity decreased in variable proportion. A second plateau was observed for more diluted suspensions (10−500 ppb), with signal intensity losses of 25%. The signal stability varies with concentration. The most diluted suspensions show poorer RSD than more concentrated ones,

which was not the case for the Ru-104 suspension when analyzed at $t = 0$. The most probable hypothesis is the appearance of coarser Ru-104 nanoparticles, whose relative importance on stability is greater at low concentration. This could not be observed by DLS, which was performed only at high concentration.

These experiments were repeated after 10 h to determine if it is possible to reach a final state. The (I_{10h}/I_0) variation curve presents the same shape as I_{2h}/I: two plateaus and a step zone. On the first plateau, points above 100% can be observed. This can be explained by either a suspension concentration due to evaporation (because the containers are maintained open for 10 h) or by the appearance of a depth-dependent concentration gradient not totally eliminated by the magnetic stirring and due to a probable flotation of some nanoparticles. The intermediate zone appears steeper than previously, with suspensions losing more than 60% of their ICP signal intensity. The second plateau is situated largely below the I_{2h}/I_0 low-concentration plateau at around 70% of signal loss. The measurements were unstable, with RSD reaching 10%.

The experiments were repeated at $t = 1$ and 5 days. The variation curves obtained were then very comparable to that observed after 10 h, when a final state had probably been reached. It is very surprising that the diluted suspension plateau did not decrease to zero with age. On the contrary, a final partition seemed to be reached between the suspensions and the vial inner surfaces when 20% of the Ti signal intensity remained.

From this set of experiments, it is possible to define a limit concentration, C^S, above which suspensions are stable with aging. In the same way, C^E can be defined as the initial concentration under which aging degradation is proportionally constant. Between C^S and C^E, an intermediate zone is found where the suspension aging evolution varies with concentration. Under these experimental conditions for Ru-104, C^S is ~7 ppm, and C^E, ~500 ppb.

Influence of Vial Volume and Ru-104 Nanoparticles Concentration on Aging Kinetic. Measurements were performed at higher PFA vials volumes (120 mL) and compared with those from the 60 mL jars (Figure 4). Similar variation curve shapes were observed. C^E and C^S remained unchanged: both limit concentration values were not volume-dependent. Nevertheless, the comparison between the 60 and 120 mL vial (I_{10h}/I_0) curves shows a shift between low-concentration plateau heights. It can then be stated that vial
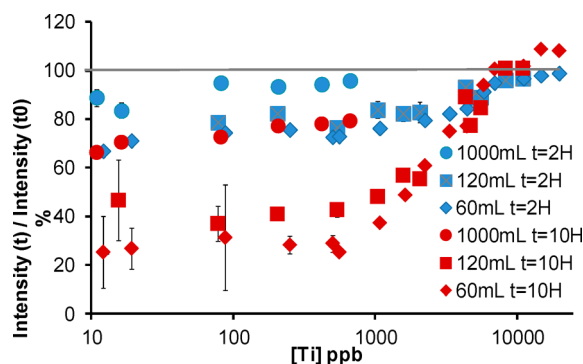
volume has an influence on the signal evolution kinetic. This is confirmed by the 1000 mL vial study, and an aging kinetic appears to be even slower. This can be explained by a lower probability for aggregates to enter into contact with the inner surface of the jar for large volume suspensions compared with smaller ones, slowing down the aging kinetic.

Behavior of Other Nanoparticles. Just as for Ru-104, the influence of the Ana-120 concentration was studied in the range of 10 ppb to 30 ppm in a set of 60 mL vials (Figure 5). The
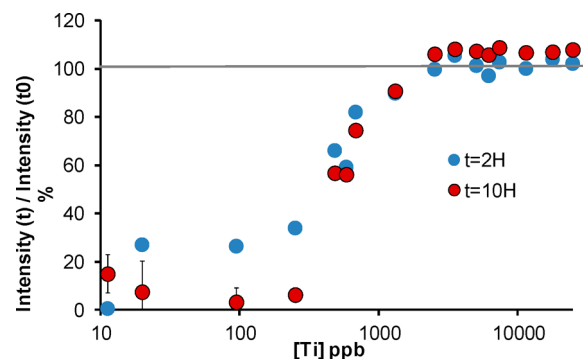

Figure 5. Influence of Ana-120 suspension concentration on signal measured at two ages (t). Experimental conditions: see Figure 3

evolution curves are similar to those for Ru-104, but with a faster aging kinetic and steeper intermediate zone. After only 2 h, the low-concentration plateau was around 30% vs 70% for Ru-104 in the same conditions. After 10 h, low-concentration signals become unstable, and it is rather impossible to make any reliable measure. The limit concentration values are very different from those for the Ru-104. The Ana-120 nanoparticles could be easily studied, the suspensions remaining stable down to 2.5 ppm against 7 ppm for Ru-104. The C^E was then 250 ppb vs 500 for Ru-104. It is difficult to explain the reason for the Ru-104 and Ana-120 difference of behavior because the nanomaterials (dispersant, coating, etc.) are not fully described.

A third nanomaterial, Ana-102 was studied at three ages (2 h, 10 h, and 1d; Supporting Information Figure S2). The first observation is the poor stability of the measures, probably because of the important size polydispersity of the Ana-102 and the presence of large aggregates. The replica number or integration time should be increased to improve the results, but they would be more difficult to compare with both Ru-104 and Ana-120. It also should be pointed out that the emission signal never exceeds 100%, unlike what is observed for the two other nanomaterials, because of a strong sedimentation not eliminated by magnetic stirring. Considering now the limit concentration values, C^E reaches 3200 ppb, far from the Ana-120 value of 250 ppb, and C^S was 7 ppm, as for Ru-104.

The C^E discrepancy observed among the three nanomaterials cannot be explained by their mineral form (anatase or rutile) or by their size difference. Expressed in aggregate number by liter and considering the average aggregate size measured by DLS after 2 h, C^E was 2.5×10^{12}, 4×10^{13}, and 6×10^9 for Ru-104, Ana-120, and Ana-102, respectively. The discrepancy between C^E values is more probably due to their surface hydrophobicity difference. As already mentioned, Ana-120 is sold as a suspension and contains a dispersant. It is clearly the most hydrophilic; it does not aggregate with time (Supporting Information Figure S1). Ru-104 is described as hydrophilic by its supplier. Its TGA mass loss reported elsewhere[16] reaches

Figure 4. Influence of Ru-104 suspension concentrations on signal measured at two suspension ages (t) and for three PFA jar sizes. For other conditions, see Figure 3.

2%. Ana-102 is a high-purity anatase that is very probably more hydrophobic, and no loss was observed by TGA.[16]

Focusing now on the aging kinetic, it appears to be slower for Ana-102 compared with the two others, confirming the relation between the nanoparticles' size and aging kinetic.

The fourth nanomaterial described here, Ana-101, which showed size distribution characteristics and a ζ-potential close to Ana-102 but a very large porosity, was also studied. The results obtained were very similar to the Ana 101, with a strong sedimentation and slow aging degradation (C^E, 3600 ppb; C^S, 10 ppm). No noticeable effect of porosity on ICP signal evolution was highlighted.

Stability Regimes. Above the C^S concentration value, suspensions were stable, even if the ICP measurement could be biased by the presence of a depth-dependent concentration gradient. Below the equilibrium concentration, C^E, the signal loss was at a maximum, and a final repartition was reached between the container and the suspension. Between these two regimes, the suspension aging varied with concentration. C^E and C^S depend on the nanoparticles' characteristics and medium, whereas the evolution kinetic is volume-dependent.

The existence of two plateaus can be ascribed to three different phenomena. First, the particles have a tendency to adsorb onto the walls of the containers. This depends on the type of particles and it takes time. The total amount required to saturate the walls has to be compared with the total amount of particles available in the suspension. When the concentration is high, the ratio is very small, and there is a weak "wall effect" on the measured value. When the concentration is lower, the kinetics of the adsorption have to be taken into account, and there is a strong "wall effect". When the concentration is low, it also takes time to diffuse and adsorb onto the walls. This explains why the plateau at low concentration takes some time to appear (typically 2 h).

The existence of a plateau itself is a little more subtle to explain. As seen in Figure 4, when time increases, the plateau decreases together with a lower limit concentration C^E. One possible explanation could be that the "stickiness" of the nanoparticles toward the wall is not homogeneous, and some fractions are sticking less easily to the walls. With time, this fraction increases, but at a given time, the plateau (versus concentration) corresponds to a fraction not yet able to adsorb.

All the suspensions studied showed C^S values above 1 ppm. These values are not really compatible with ICPOES and even less so with ICPMS ranges of analysis, which are more often in the parts-per-trillion to parts-per-billion range. Even more disturbing is the fact that the concentration of TiO_2 in the environment is estimated at around a few tens of parts per billion, so several orders of magnitude under the C^S value. To circumvent the problem, it is possible to work on large volumes of sample (at least 1 L) that should be analyzed as soon as possible after the sampling. Practically, it is conceivable to sample and treat large volumes of river water but difficult to analyze them rapidly (preferably within 2 h). A better solution would be to preserve the samples at least 24 h and also to suspend the nanoparticles again in a quantitative and reproducible manner for analysis.

Sonication. Most of the articles dealing with the analysis of nanoparticles in suspension report the use of sonication to break aggregates. Unfortunately, details and performances of this sample treatment are never described, despite the fact that many parameters govern sonication.[19] Table 2 reports typical results of the first experiments performed here. A Ru-104 suspension was divided into five identical vials. The vials were sonicated for 5 min in a bath and analyzed at three different ages after sonication. Signal repeatabilities remained stable (RSD < 4%). In contrast, interval reproducibilities dramatically decreased after sonication, reaching around 27% just 45 min after the 5 min sonication process. This result illustrates what is generally observed. Sonication improves average signal intensities, reaching the initial value, but this improvement is very transitory. In this example, sonication lasted only 5 min. In most cases, increasing its duration degrades the interval reproducibility even further. To solve this difficulty, a systematic and simplified study is then needed.

Various parameters governing sonication were tested: frequency (37, 80 kHz), duration, sonication mode (pulse mode to avoid sample heating, sweep mode for a better sound wave space distribution in the bath or degas mode), and bath temperature. Because suspensions evolve largely after sonication, samples were measured during sonication. Low frequency gave better results in terms of signal intensity, showing that it is important for the sound wave to penetrate the suspension. It could be relevant to even lower sound frequency. Unfortunately, sonication devices working at the lowest frequency (20 kHz) use a technology based on immersion probes made of titanium, which pollutes the TiO_2 suspension by erosion. Bath sonication is thus the only option. Pulse and sweep modes give similar results and degas shows no effect.

Bath temperature plays a great role. Its influence on the ICP signal intensity was studied between 0 and 60 °C. The results obtained on two sets of five vials filled with a 1-day-old Ru-104 suspension (400 ppb in pH 1.5 nitric acid, 60 mL PFA vials) showed that the ICP signal could be improved to 30% when sonication was performed in an ice bath instead of water. To avoid suspension heating as much as possible, the PFA vials were then replaced by 100-mL glass Erlenmeyers, and sonication was performed in a periodically renewed ice and water bath. Duration is also an important parameter. If the duration is too short, homogenization is not optimal and Ti is under-evaluated. In contrast, when sonication is too long, the ICP signal tends to decrease. There is then a nonpredictable optimum sonication time, depending on various parameters, such as the suspension's age and volume and the sonication power or sample position in the sonication bath.[19]

It can be hypothesized that free radicals produced by sonication influence nanoparticles adsorption on vial walls. These unwanted reactions are favored at high temperature. The TiO_2 surface is also known to produce reactive oxygen species (ROS),[20] specifically, radical hydroxyls $OH^\bullet$ and superoxide anions $O_2^{\bullet-}$. To eliminate the interfering effect of ROS, isopropyl alcohol, a free radical inhibitor, was added to the suspensions.[21] It should be pointed out that this addition must be realized on samples and standards, small amounts of organic solvents classically amplifying ICP signals. The addition of a free-radical inhibitor resulted in a great simplification of the sonication process. Unpredictable optimal sonication times were no longer observed. Instead, the ICP signals increased with sonication duration until they reach a plateau, indicating that homogenization was finished (even if not total). The interval reproducibility was also improved. For example, a suspension divided into four glass Erlenmeyers sonicated at low temperature for 1 h in the presence of isopropyl alcohol gave an interval reproducibility of 1.7%. Under the same conditions, except for the free-radical inhibitor, which was not present, the interval reproducibility measure on a set of five samples

exceeded 8%. The combination of low bath temperature and free-radical inhibitor addition allowed performance of sonication under sufficiently soft conditions to probably break some aggregates but, most of all, to homogenize the suspensions without generating unwanted radical reactions. Elements of this sample treatment procedure are the object of a patent.[22]

Suspensions' Behavior in River Water Medium. We focus here on the Seine river water, which showed a neutral pH (pH 8). In this medium, TiO_2 nanoparticle suspensions were not supposed to be stable. When poured into river water, the nanoparticles immediately aggregated. Various studies were conducted on Ana-120 in this medium. Results were similar to what is observed at pH 1.5. Here also, the (I_t/I_0) curves showed two plateaus separated by an intermediate zone. The main difference between river water and pH 1.5 is the measurement stability. The RSDs were very poor, and they could easily reach several tens of percent. Acidification (nitric acid, hydrochloric acid, or aqua regia) did not really show an advantageous effect, except to minimize nebulization clogging and spray chamber washout. With HCl and aqua regia (10% in river water), the C^S constant measured by ICPOES was then above 10 ppm, and the C^E was around 2 ppm. Real environmental samples were thus situated on the low-concentration plateau, where the signal loss is at a maximum. Samples should then be treated by soft sonication before and during analysis.

External Calibration and Internal Standard. ICPMS suspensionn measurements were calibrated with standard titanium solution and the addition of an internal standard (Co). Internal standard addition is an interesting point because the adsorption of elements on the surface of titanium nanoparticles is often reported. The internal standard is here introduced to control ICPMS instrumental deviation and sonication efficiency but not to testify to its chemical adsorption on the nanoparticles' surfaces.[23] A set of glass Erlenmeyers was filled with 250 ppb Ana-120 suspended in filtered river water. The river water was acidified by aqua regia and contained isopropyl alcohol. Suspensions were stocked refrigerated for 3 days. The internal standard was added before storage in some Erlenmeyers and just before analysis in the others. Samples were sonicated before and during analysis. When the internal standard was introduced just before analysis, deviations between measured and expected values varied between 15 and 35%. Suspensions in which internal standard was added before storage could be more reliably measured; deviation between measures and expected values was below 5%. The addition of internal standard before storage allows correcting not only instrumental deviation but also a probable lack of sonication efficiency.

To validate this procedure, Ana-120 suspensions with concentrations ranging between 5 and 100 ppb were studied after 4 days of storage. Internal standard was added before storage, and its amount was identical in all the samples. Its concentration was fixed at 10 ppb. The Ti/Co ratios then varied between 0.5 and 10. The results are shown in Table 3. There is no relation between the quantity of the internal standard and the amount of nanoparticles. The deviation between expected values and measures are here also better than 5% for all samples, whatever the nanoparticles amount.

Seine River Total Titanium Determination. To validate this study, a large volume of Seine River water (5 L) was sampled and analyzed both by ICPOES after titanium solubilization and by ICPMS as described above. The sample was transferred as rapidly as possible into the laboratory

Table 3. Concentrations of Ti Measured by ICPMS on 4-Day Old Suspensions of Ana-120 in Nitric Acid and Isopropyl Alcohol 1% (v/v)[a]

sample	expected value Ti (ppb)	measured value Ti (ppb) ± RSD%	difference (%)
5 ppb v1	5.2	4.9 ± 5.3%	−6
5 ppb v2	5.2	5.4 ± 3%	3.8
25 ppb v1	25.9	25 ± 0.7%	−3.7
25 ppb v2	25.9	24.5 ± 1.5%	−5.5
50 ppb v1	51.7	49.3 ± 1%	−4.7
50 ppb v2	51.7	47.5 ± 1%	−8.2
100 ppb v1	105.6	102.7 ± 1.2%	−2.8

[a]The internal standard (Co) was added before storage. [Co] = 10 ppb. The samples were sonicated before and during measurement.

(typically 2 h). A first aliquot of the sample was put aside for titanium mineralization as described here. The amount of titanium was measured by ICPOES by the standard addition method. The amount of titanium found by mineralization was 48.2 ppb. A second aliquot of the river water sample was used for a direct suspension measure. Isopropyl alcohol (1% v) was added to 0.5 L of sample in a glass container. The container was then sonicated in an ice bath for 10 min, as described. The sample was filtered on a 320 μm nylon filter to avoid nebulizer clogging, removing medium sand and coarser particles.[24] It should be pointed out that this first sonication, breaking coarser particles, induces an increase in the measured titanium of around 30%. This confirms the adsorption of titanium on nondissolved materials. These nondissolved materials may be other inorganic materials, such as clays, but more probably are of organic origin, such as humic acids. These mixed large aggregates of tens of micrometers in size include mineral particles, such as TiO_2, that are quite loosely bound, and a soft sonication reduces their size to around 1 μm (typically the size of solvent shearing imposed by ultrasound), much under the 320 μm limit of the nylon filter. Co was added as the internal standard, and a suspension of 90 mL was stored in a refrigerated glass container. A day later, the sample was analyzed under sonication after acidification by aqua regia (2%). The measurement was realized by ICPMS with the standard addition method (Supporting Information Figure S3). The amount of titanium found by direct measurement was 48.7 ppb. The difference between the mineralization method and direct suspension was 1%. This very good agreement between the two methods validates the procedure, at least for 24 h storage. It should be added that the amount of titanium found in the Seine River sampled inside the city of Paris is also coherent with measurements previously realized in Great Britain[25] in various river waters, where the average value found after filtration at 0.45 μm was 2.1 ppb.

■ CONCLUSION

The study shows the existence of rather high concentration levels (several ppm) below which the determination of TiO_2 nanoparticles is hindered by aging phenomena classically affecting with such an amplitude solutions at levels below parts per billion. If the TiO_2 nanoparticle behavior is confirmed on other nanomaterials, it could be an explanation of the discrepancies observed in many nanoparticle studies. This description was realized by plasma spectrometry (ICPMS and ICPOES), which appear to be relevant techniques for studying

the behavior of suspensions in a large range of concentration[26] and for reliably measuring nanoparticles in suspension after adequate sample treatment. Plasma spectrometry may become a technique that is complementary to the classical DLS, SAXS, etc., which are applied to nanoparticles at high concentrations (above C^S). They can reveal important information, such as elemental composition and size distributions, using special modes, that is, single particle counting or monodisperse microdroplet carrying introduction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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