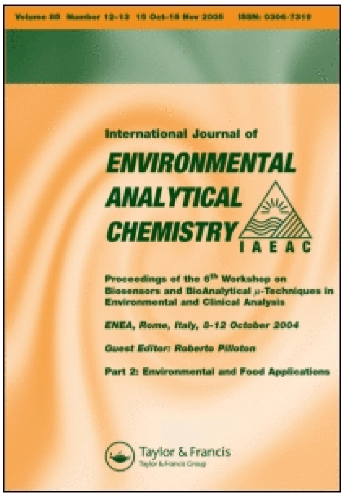

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Chemical Composition Determination of Suspended Mineral Particles and Colloidal Fractions of River Samples

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CHEMICAL COMPOSITION DETERMINATION OF SUSPENDED MINERAL PARTICLES AND COLLOIDAL FRACTIONS OF RIVER SAMPLES

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In this paper the technique and procedure were developed to determine the chemical compositions of suspended mineral particles in the different fractions of river samples by gravimetry, aqua rega–HF–H_3BO_3 digestion and ICP–AES analysis. Particulate Si, Al, Ca, Fe, Mg and Mn in the different fractions can be determined simutaneously, precisely and accurately with a simple procedure at very low concentrations. The loss of Si in the digestion was not observed. The presence of boric acid did not cause any interference in the analysis. The comparisons between digested and non-digested particles in the fractions of diameters > 3µm, < 2–3 µm and < 0.8 µm were made. A negative error occurred in non digested particles.

KEY WORDS: River waters, suspended particles, particle size fractionation, ICP–AES, inorganic colloids, metals.

INTRODUCTION

To evaluate the impact of pollutions in surface water systems it is essential to know the physical and chemical properties of suspended particles in the systems, i.e. their size distribution and the chemical compositions of different fractions. Particles, especially submicron particles, in the river waters are of particular importance for understanding the fate of trace metals and organic pollutants in natural waters because they provide large reactive surface to interact with pollutants and eventually bring them to the sediment by coagulation and sedimentation[1,2]. The surfaces of different particles have different chemical and physical properties and morphologies. Therefore their capacities in the regulation of the concentrations of pollutants vary greatly[3,4].

Though the importance of physicochemical characterization of particles is well known, few studies have been done in this field. Most of chemical characterization of inorganic particles in the suspended water samples is done with TEM–EDS (Transmission Electron Microscopy–Energy Dispersive Spectroscopy)[5,6,7] and other techniques, such as EELS (Electron Energy Loss Spectrometry) and LAMMA (Laser Microscopy Mass Analysis)[5,8]. All these techniques allow to analyze the chemical compositions of individual particles, but they do not provide statistically reliable

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information on the whole of the particles present in a suspension, within a reasonable period of working time, and at a reasonable cost. Until recently the chemical compositions of total suspended mineral particles, particularly with particle size close to or smaller than 1 μm are rarely studied in surface waters[5,9,10]. Major difficulties are (1) the low concentrations of suspended particles, particularly the small size particles (≤ 1 μm), (2) the chemical heterogeneity of natural colloidal systems, and (3) the artifacts in fractionation of particles by sizes, due to aggregation and biodegradation[9].

In this work, the attention was particularly focused on the chemical analysis of the major elements Si, Al, Ca, Mg and minor elements Fe and Mn in the suspended mineral particles in the different size fractions of the Arve River (Geneva, Switzerland). The dominant mineral particles in the Arve River are sands, clay debris, and calcium and magnesium carbonate. The difficulty in analyses of particulate Si and Al elements is the refractory nature of the corresponding minerals (clays). The conventional fusion digestion techniques for geological samples can not be used due to low particle concentrations in river waters and particularly in their subfractions. Bernas[11] was one of the pioneers who successfully measured Si and Al in rock samples by atomic absorption spectrometry after hydrofluoric acid digestion and boric acid complexation with ecessive HF. 8 years later, using a modified method Eggimann and Betzer[10] achieved the analyses of Si, Al, Ca, Fe, Mg and Mn in the particulate phase in the ocean. However they used a quite complicated sample digestion procedure (adding HCl, HNO_3 and HF successively and cooling at -40°C after each acid attack). They did not use H_3BO_3 because the measurements showed that even small amounts of H_3BO_3 caused intense light scattering which precluded the background correction in AAS analysis. They found that the presence of boric acid caused significant interferences in the measurement of Al, Fe and Mn in heated graphite atomizer. They analyzed Si by colorimetry because they found that volatility of SiF_4 precluded any silicon measurement by flamless atomic absorption. They measured Fe, Al and Mn with flameless atomic absorption and Ca and Mg with air–acetylene flame atomic absorption.

In the present paper, we have developed a complete procedure to analyze chemical compositions of total particles in different fractions of the suspensions of rive waters. This procedure includes particle fractionation by sedimentation and filtration, total particle mass analyses (in different fractions of suspension) by gravimetry, sample digestion by aqua rega–HF–H_3BO_3 and simutanously analysis of the 6 above mentioned elements by ICP—AES. The interference of the presence of H_3BO_3 found by Eggimann and Betzer[10] was not observed in our analyses; the loss of silicon at high temperature in plasma torch was not found either. In a closed system the volatile SiF_4 should be recovered into the solution due to the following reaction[12]:

$$3\ SiF_4 + (x + 2)\ H_2O = 2\ H_2SiF_6 + SiO_2.\ xH_2O$$

The amorphous silicon dioxide is easily dissolved in an acidic medium.

EXPERIMENTAL

Experimental facilities

The following apparatus and reagents were used:

- ICP Spectrometer Perkin–Elmer, "Plasma 1000";
- Ultra sonication probe (Branson sonifier 250, equipped with a titanium tip, maximum output power 200W, maximum frequency 20 KHz);

- Plexiglass filtration cells (Φ 47 and 90 mm homemade);
- Nuclepore polycarbonate membranes (0.05 μm and 0.8 μm in pore sizes, and 47 mm and 90 mm in diameters respectively);
- Balance: Mettler H51AR (d=0.01 mg);
- Teflon bombs (50 cm^3),Techniverre (France)
- High density polyethylene (PE) and polypropylene (PP) graded flasks or tubes;
- Standard sediment reference MESS–1 (NRC of Canada);
- All the reagents (HCl 30%, HNO_3 65% and HF 40%) used in the sample digestion and standard solution preparation were suprapur produced by Merck, only H_3BO_3 is crystal Gr.
- Milli-Q double deionized and 0.2 μm filtered water.

Sample fractionation and total particle mass (TPM) analysis by gravimetry

The fractionation procedure is described by Perret *et al.*[13] As soon as the river water (35 liters) was collected, one fraction (1.0 liter) of this water was taken and stored at 5±2°C in the dark as raw water fraction. The rest of the sample was allowed to sediment in a 30–Liter isothermostatic tank for 2 or 3 hours in order to eliminate most of the largest particles ($\Phi > 2 - 3$ μm, $\rho \simeq 2.7$) from the top sedimented water. The supernatant was collected evenly from the same layer (1.0 – 2.5 cm from the top level) by a peristaltic pump[13]. One portion of the supernatant (500 cm^3) was kept as the sedimented fraction. The rest of the sample (1.0 liter) was subjected to 0.8 μm filtration. 600 cm^3 of the filtrate was obtained as the 0.8 μm fraction.

The total particle masses of the above fractions as well as those of the raw water sample were obtained by filtration on 0.05 μm (Φ 47 mm) Nuclepore polycarbonate membrane with a pressure (N_2) 2 atm. and a maximum flow–rate to maximize coagulation at the filter surface in order to collect the particles smaller than the pore size of the filter. At the end of filtration, the filter was gently rinsed with Milli–Q water, and filtration was performed again to dryness in order to avoid contamination from Ca^{2+} and Mg^{2+}. The filter was dried in oven at 60°C and weighed. The total particle mass concentration was obtained by subtracting the weight of the filter before filtration. The total particle concentrations in different fractions of the Arve River samples of March 17, April 28 and May 1 were summarized in Table 1. It is important to note that the particle

Table 1 Total particle mass concentrations in the raw water and fractionated samples of Arve River

date	*fraction*	*size (Φ) (μm)*	*replicate*	*average (mg.dm^{-3})*	*CV (%)*
17/03/1992	raw water		3	58.02	2.56
	2hr–sed.water	< 2 – 3	3	10.07	0.95
28/04/1992	raw water		4	233.01	3.57
	2hr–sed. water	< 2 – 3	4	27.23	1.77
	3hr–sed. water	< 2 – 3	4	25.57	2.03
01/05/1992	raw water		4	50.34	2.78
	3hr–sed. water	< 2 – 3	4	9.60	4.48
	0.8 μm filtrate	< 0.8	4	2.65	4.10

mass after 2h and 3 h sedimentation, represents only 10 ~ 20% of the mass in the raw water, and that the mass of submicron particles represents only a few percent of the mass of the raw water. This has been found in other surface water samples[14].

One of the four filters in each fraction of April 28 and May 1 was kept for non–digestion test. The other three filters in each fraction were manipulated as described below.

Particle digestion

The filter was rinsed and soaked in 3–5 cm^3 5% HNO_3 acid in a 20 cm^3 graded high density polyethylene tube. Then it was sonicated with a sonication probe using an output power 50W for 3 min. The particle was transferred into a 50 cm^3 Teflon bomb. The operation was repeated 1 – 2 times with 3 cm^3 Milli-Q water to recover all particles on the filter. The Teflon bomb (without cap) was put on a hot plate to evaporate water to complete dryness at a temperature below the boiling point (~ 80°C). Depending on the quantities of particles and organic materials in the water sample, 10 to 500 µL of freshly prepared aqua regia was added. The cap was closed and the bomb was heated on the hot plate in order to destroy all the organic materials. A complete digestion of organic matter can be confirmed by the disappearance of any black substance in the solution. 0.1–2.5 cm^3 40% HF was pipetted into the sample The cap was tightened manually. The sample was digested at 110°C in a common laboratory dry oven overnight. After digestion, the bomb was cooled down by puting it in a refrigerator. When it was cold, 0.05–2.0 grams of H_3BO_3 was added to complex the excess of HF acid under agitation. After about 10 minutes of reaction, the solution was carefully transferred into an acid (3M HCl–1M HNO_3) cleaned flask. Any solid minerals should be dissolved at this step.

Possible contaminations from the ultrasonic probe tip and membrane were also studied by sonicating 5 pieces of blank Nuclepore filters (0.5 µm, Φ 47 mm) in 5% HNO_3 acid as other filters containing the particles. The possible contamination from reagents was also checked by a triplicate of blank measurements. 0.5 cm^3 aqua regia, 2.5 cm^3 40% HF and 2.0 gram H_3BO_3 and 5 cm^3 of 5% HNO_3 were added as other digested samples and the solutions were diluted to 50.0 cm^3 before the analysis. The results did not show any contamination of the 6 measured elements, neither from ultrasonic probe tip nor from the reagents and the membranes. The possible interference from H_3BO_3 was studied by comparing the emission intensities of 6 elements between the standard solutions with and without H_3BO_3. No influence was found. However all standard solutions were prepared with the same amount of H_3BO_3 as in the sample solution, and the standard solutions were prepared as close as possible to the concentrations of sample solutions.

ICP working conditions were as follows: plasma source unit = frequency 27.12 MHz; power = 1000 W; gas = argon; nebulization flow = 1.00 $L.min^{-1}$; auxiliary flow = 1.0 $L.min^{-1}$; plasma flow = 15 $L.min^{-1}$; pump rate (sample take up rate) = 1.0 $cm^3.min^{-1}$; equilibrium time = 15 sec.; viewing height (compromised for 6 elements) = 15 mm; type of torch = quartz; detection wavelengths (nm) = Ca 393.366, Al 396.152, Fe 238. 204, Mg 279.553, Mn 257.610, Si 251.611.

Analysis of standard sediment reference

A standard sediment MESS–1 (NRC of Canada) was used to check the digestion method. 30.0 mg and 200.0 mg of MESS–1 sediment was weighed precisely in triplicate

Table 2 ICP analytical results of standard sediment MESS–1 (NRC of Canada)

	Fe_2O_3	Al_2O_3	SiO_2	CaO	MgO	Mn
Cited value (mg/100 mg)	4.36	11.03	67.50	0.674	1.44	513 (mg/kg)
CI/$_{CL95\%}$	0.25	0.38	1.90	0.064	0.09	25
Analysis of 30.0 mg MESS–1 Sediment						
Measured (mg/100 mg)	4.39	10.86	67.51	0.693	1.37	494.4 (mg/kg)
S.D.	0.08	0.06	1.55	0.02	0.03	19.28
CI/$_{CL95\%}^{+}$	0.20	0.15	3.85	0.05	0.07	48
Relative error (%)	0.64	- 1.54	0.01	2.82	- 4.86	- 3.6
Analysis of 200.0 mg MESS–1 Sediment						
Measured (mg/100 mg)	4.37	10.99	65.20	0.686	1.36	500 (mg/kg)
S.D.	0.08	0.12	2.15	0.02	0.01	0.0
CI/$_{CL95\%}^{+}$	0.20	0.30	5.34	0.05	0.02	0.0
Relative error (%)	0.23	- 0.36	- 3.41	1.78	- 5.56	- 2.53

[+] CI = Confidence Interval; CL = Confidence Level, here the values are the confidence intervals of the triplicate measurement when the confidence level is 95% ($\pm ts/\sqrt{N}$, t = 4.3, N = 3).

respectively and digested as described above. ICP analyses were done in quadruplicate for each element. The results are given in Table 2.

The analyses for the 6 elements agreed well with the reference values. Silicium did not show any significant loss at this sample quantity. However the analysis of Si showed a memory effect, especially when Si concentration was high. A careful washing of the aspiration system before analysis and starting analysis with a sample of lower Si concentration can eliminate this problem.

RESULTS OF THE ANALYSES OF THE ARVE WATER SAMPLES BY ICP

Table 3 shows the average mass concentrations of each type of mineral particles and the total particle mass concentrations TPM (mg.dm^{-3}) obtained from three filters, either computed from ICP results (TPM_{ICP}) or measured by gravimetry ($TPM_{grav.}$). TPM_{ICP} are calculated on the basis of the simplified mineral forms (oxides) in order to be able to compare the total particle mass obtained by gravimetry.

These results show that coefficient of variation (CV%) of TPM_{ICP} are normally close to or slightly higher than those of TPM_{grav} (Table 1), which means that the errors are mainly introduced from filtration which largely depends on the homogeneity of the particles and the mass concentrations in the water samples. The errors introduced in other operations, e.g. particle digestion (CV = 0.6 – 2%), solution preparation (CV = 0.1 – 0.2%) and ICP analysis (CV = 0.2 – 1%) are relatively small.

The relative difference between TPM_{ICP} and $TPM_{grav.}$, $\Delta\% = (TPM_{ICP} - TPM_{grav.})/TPM_{grav.} \times 100$ (eq. 1), is constantly about –15%. This is probably due to the chosen simplified mineral compositions in the estimation of TPM_{ICP}

Table 3 Evaluation of quality of the analysis

date	SiO_2	$CaCO_3$	Al_2O_3	Fe_2O_3	$MgCO_3$	MnO_2	TPM_{ICP}	$TPM_{gra.}$	Δ%
17/03/92									
				raw water sample					
X̄ (mg.dm^{-3})	21.91	15.75	6.15	2.39	2.35	67.7 x 10^{-3}	48.63	58.02	- 16.2
CV (%)	5.48	2.11	1.75	0.72	1.73	2.56	3.43	2.66	
				2hr–sed. water sample					
X̄ (mg.dm^{-3})	3.51	2.34	1.49	0.51	0.43	11.9 x 10^{-3}	8.29	10.07	- 17.7
CV (%)3.56	3.56	2.47	1.16	3.90	0.00	2.73	1.51	0.95	
28/04/92									
				raw water sample					
X̄ (mg.dm^{-3})	86.12	68.83	26.17	10.12	11.59	0.27	203.10	233.25	- 13.0
CV (%)	8.13	5.84	4.86	4.40	4.40	8.63	5.94	4.36	
				2hr–sed. water sample					
X̄ (mg.dm^{-3})	9.27	6.79	4.72	1.43	1.28	0.033	23.52	27.24	- 13.6
CV (%)	1.80	1.45	2.72	2.33	1.35	1.75	1.63	2.16	
				3hr–sed. water sample					
X̄ (mg.dm^{-3})	8.66	6.39	4.52	1.37	1.25	0.030	22.21	25.56	- 13.3
CV (%)	2.89	4.53	3.01	2.56	5.45	4.92	3.40	2.54	
01/05/92									
				raw water sample					
X̄ (mg.dm^{-3})	18.12	15.49	5.65	2.25	2.29	57.9 x 10^{-3}	43.86	50.01	- 12.4
CV (%)	1.11	3.28	4.29	4.11	4.03	3.27	4.31	3.02	
				3hr–sed. water sample					
X̄ (mg.dm^{-3})	2.98	2.61	1.40	0.47	0.41	12.2 x 10^{-3}	7.88	9.49	- 16.9
CV (%)	3.87	4.78	6.35	7.47	8.45	5.68	4.65	4.77	
				0.8 μm filtrate					
X̄ (mg.dm^{-3})	0.72	0.83	0.44	0.15	0.15	3.9 x 10^{-3}	2.29	2.65	- 15.1
CV (%)	5.01	2.78	5.72	11.6	11.6	2.98	3.78	5.03	

(X̄ = the average of a triplicate measurement, i.e. the particles are from three filtrations; Δ% is defined in Eq.1.; CV% is the coefficient of variation for triplicate measurements)

DISCUSSION

Chemical composition of fractions

The percentage of each type of mineral particles in different fractions compared to the $TPM_{grav.}$ in the raw water samples are given in Table 4. During 2 or 3 hours of sedimentation, the concentrations of each of the 6 components has decreased by about 80% ~ 90% due to the settling of the largest particles. One hour more sedimentation did not remove more than 1% (in mass) of each type of particles. Therefore for the purpose of fractionation of particles by size the 2 hour sedimentation is generally sufficient. This has also been shown by light scattering and gravimetric measurement[9,13].

From the results in Table 3, the percentages of each type of element in their per se fractions can be also obtained. The data are given in Table 5 as follows: $C\%_R$ (M), $C\%_{2S}$ (M), $C\%_{3S}$ (M) and $C\%_{0.8}$ (M) represent the relative molar concentration percentages of elements in raw water sample, 2 hour and 3 hour sedimented water samples and 0.8 µm filtrate water sample respectively. For instance for Si, $C\%_{2S(Si)} = C_{2S(Si)} / \sum C_{2S}. \times 100$, where $C_{2S(Si)}$ = the molar concentration of Si in 2h-sedimented sample, and $\sum C_{2S}$ is the sum of molar concentrations of the 6 elements in the 2h-sedimented sample.

The results in Table 5 allows to evaluate the possible change in proportion of each element from one size fraction to another. For instance, the proportions of calcium and silicium particles in the sedimented water samples were reduced by 7 – 18% and 10% respectively; while the proportions of aluminium and iron particles were increased by about 30 – 50% and 10 – 26% respectively compared to those in the raw samples. These changes are larger than the analytical errors included in all operations and analyses, usually less than 5 – 7 % for raw and fractionated water samples (Table 2, 3). The most significant observation however is the relative increase in proportion of Al, compared to a slight decrease of Si. This suggests that clay-silicates (represented by Al) are in smaller

Table 4 The relative percentage of each mineral particles in different fractions compared to $TPM_{grav.}$ in the raw waters.

Fraction	SiO_2 (%)	$CaCO_3$ (%)	Al_2O_3 (%)	Fe_2O_3 (%)	$MgCO_3$ (%)	MnO_2 (%)
17/03/92						
raw water	37.76	27.15	10.60	4.12	4.05	1.17
2h-sedi.	6.05	4.03	2.57	0.88	0.74	0.21
28/04/92						
raw water	36.92	29.51	11.22	4.34	4.97	1.16
2h-sedi.	3.97	2.91	2.02	0.61	0.55	0.14
3h-sedi.	3.71	2.74	1.94	0.59	0.54	0.13
01/05/92						
raw water	36.23	30.97	11.30	4.50	4.58	1.16
3h-sedi.	5.96	5.22	2.80	0.94	0.82	0.24
0.8 µm filtr.	1.44	1.66	0.88	0.30	0.30	0.08

Table 5 Percentage of each particulate element in their per se fractions

Date	*Si*	*Ca*	*Al*	*Fe*	*Mg*	*Mn*
17/03/1992						
$C\%_R$	52.5	22.1	17.3	4.2	4.0	0.11
$C\%_{2S}$	47.5	18.7	23.9	5.3	4.5	0.11
28/04/1992						
$C\%_R$	49.7	23.4	17.7	4.4	4.8	0.11
$C\%_{2S}$	44.7	19.3	26.5	5.0	4.3	0.11
$C\%_{3S}$	44.5	19.3	26.8	5.1	4.4	0.11
01/05/1992						
$C\%_R$	48.3	24.4	18.0	4.5	4.3	0.11
$C\%_{3S}$	43.5	22.8	23.9	5.2	4.5	0.12
$C\%_{0.8}$	36.6	25.0	27.0	5.8	5.5	0.13

Table 6 Relative differences (%) between digested and non digested samples of the Arve River

Sample	*Size (μm)*	*Si*	*Ca*	*Al*	*Fe*	*Mg*	*Mn*
28/04/92							
raw sample		- 73.4	2.53	- 52.9	- 21.1	- 19.5	- 6.1
2h–sed.	< 2 - 3	- 23.6	3.0	- 23.0	- 9.0	- 9.3	1.8
3h–sed.	< 2 - 3	- 25.0	- 6.0	- 27.5	- 11.8	- 15.8	3.8
01/5/92							
raw sample		- 67.0	- 2.0	- 46.9	- 18.7	- 20.4	- 0.5
3h–sed.	< 2 - 3	6.3	7.5	- 19.5	0.0	- 20.1	7.1
0.8 μm Filt.	< 0.8	- 6.7	2.1	- 34.1	- 14.4	- 50.0	- 7.0

size fractions than calcium carbonate and silica, and that the latter may represent a significant fraction of particulate Si.

Comparison between digested and non–digested samples

In order to simplify analytical procedures, several authors have studied the atomization yield of particulate matter directly with ICP. Sugimae and Mizoguchi[15] found that the yield for air–borne particles depends on their sizes. Saba *et al.*[16] have indicated that the atomization yield is also influenced by the yield of nebulization of the ICP system. Ambe and Nishikawa[17] have found that the emission yield were 80% for iron and aluminum oxide particles of 0.4 ~ 1 μm, but only 17% for particles > 8 μm. Lieser *et al.*[18] claimed that atomization of Cs, Sr, Pb, Ac and Th associated with particles (in groundwater) by graphite furnace in electrothermal atomic absorption spectrometry was incomplete, whereas at a high temperature in an inductively coupled plasma, elemental composition of fine filtered colloids (0.002 ~ 0.45 μm) can be atomized directly without digestion.

In the present study, non digested particles dated on April 28 and on May 1 were measured by ICP and the results are compared with the averages of 3 digested samples. The particles on all of the filters were collected by sonication in 5% HNO_3 Milli–Q water solution as discussed before. The solutions were diluted with 5% HNO_3 to the same volumes as the volumes of their corresponding digested samples before ICP analysis. The solutions containing non–digested particles were directly introduced into the plasma and measured under the same conditions as the digested sample solutions. In Table 6 the comparisons between digested and non digested samples (in mole.dm^{-3}) are presented.

The total particle masses presented in Table 1 indicate that the mass concentrations in the sample of April 28 were much higher than those of May 1. The first sample was collected immediately after a storm; therefore the percentage of large particles was also high. The data show that the absence of digestion may introduce large errors in analysis of Si, Al, Mg and Fe, and of Si, Al and Mg in sedimented water. The measurement suggests that the most problematic particle types are clay silicates. The negative error of 0.8 μm filters should be interpreted with caution. This error might be due to the incomplete recovery of particles from the filter by sonication and the slight variation of sonication conditions from one sample to another. In any case, caution must be given when analyzing particles without digestion, even for submicron particles.

CONCLUSIONS

This method presented here has advantage of allowing the analysis of Si and Al quantitatively at very low particle concentrations. It combines the particle total mass analysis by gravimetry and elementary analysis of particulate by ICP, which allows to evaluate the errors included in sample treatment and ICP analysis, as well as to evaluate the percentages of each mineral particles related to the total particle mass and provides very important information for the interpretation of the properties of different types of suspended mineral particles in different size fractions. This method is also simple, fast and free from contaminations from other dissolved elements, such as Ca^{2+} and Mg^{2+} in the river water samples. The accuracy and precision of this method are satisfactory.

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