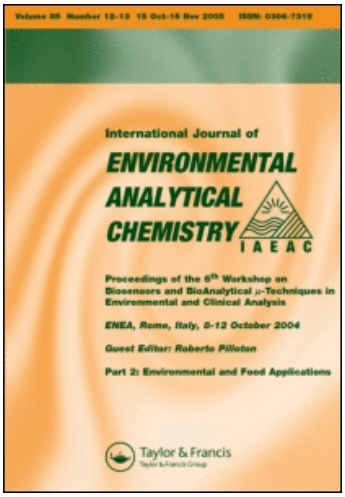

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Improved Determination of Aluminium Species in Waters Using FIA Separation/Fluorimetric Detection Techniques

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IMPROVED DETERMINATION OF ALUMINIUM SPECIES IN WATERS USING FIA SEPARATION/FLUORIMETRIC DETECTION TECHNIQUES

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A Flow Injection fluorimetric detection system, based on the reaction between aluminum and 8-hydroxyquinoline-5-sulphonic acid (8-HQS) in a micellar medium (cetyltrimethylammonium bromide (CTAB)) has been incorporated into the Driscoll fractionation method for the speciation of aluminium in waters.

Improved analytical performance over a standard batch Driscoll/Pyrocatechol Violet (PCV) method is demonstrated. Detection limits (0.9 $\mu g\ l^{-1}$), speed of analysis (20 s), linear range (0-10,000 $\mu g\ l^{-1}$), and sample volume (100 μl) are all superior to the batch PCV technique. A serious positive interference from Zinc, occurring in the 8-HQS method, has been overcome by the addition of 0.1% m/v 1,10 phenanthroline to the post-column reagent.

Good agreement between the conventional batch technique and our continuous flow determination for the important labile monomeric aluminium fraction in a series of waters has been demonstrated.

KEYWORDS: Aluminium speciation, 8-hydroxyquinoline-5-sulphonic acid, micelles, Driscoll/Pyrocatechol Violet, water.

INTRODUCTION

Although being one of the most common elements in the lithosphere, aluminium has only captured the attention of the scientific community as to its possible toxicity to a large variety of flora and fauna, including humans, within the last 15 years or so.

Aluminium toxicity has been given a high profile from an environmental view point with the recognition that "acid rain" mobilizes aluminium from poorly buffered soils into the aquatic environment [1]. The acidification of fresh water lakes and rivers in the U.S.A., Canada, and particularly the Scandinavian countries, and the subsequent rise in dissolved aluminium levels, has been linked to the decline in fish numbers, and in some cases the total elimination of entire fish populations [2-4].

Aluminium toxicity in aquatic systems is still a controversial topic, though several

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workers have demonstrated that the hydroxy species $Al(OH)_2^+$ [2, 5] and $Al(OH)^{2+}$ [6] are the toxic forms to fish. However, the toxicity and presence of these species are regulated by a number of factors such as water pH, aluminium concentration, presence of competing ligands such as F^- or organic acids, calcium concentration and species of fish.

These aluminium hydroxy species are thought to affect fish in two major toxicological ways. Firstly, insoluble aluminium hydroxide species may form, which could clog the gills of fish, thereby inhibiting proper respiratory function. Secondly, at even more modest aluminium levels (<50 $\mu g\ l^{-1}$), in waters with a low calcium content, fish can experience difficulty in maintaining their normal osmoregulatory balance and exhibit low Cl^- plasma concentrations [7].

No direct, specific method for the separation and individual quantification of those two more toxic species ($Al(OH)_2^+$ and $Al(OH)^{2+}$) exist at the present time. However, a number of fractionation procedures have been developed over the last decade to operationally distinguish between the various aqueous forms of aluminium. These methods include dialysis [8], ion-exchange, both batch [9] and column [2], HPLC [10], F^- ion-selective electrode [8], NMR [11], specific extraction [12], filtration [13] and computational techniques [14].

Perhaps the most popular of these methods today are those which can be called "Driscoll" methods. These are based around a cation ion-exchange column containing the resin Amberlite IR-120 [1, 2, 15]. This fractionation scheme directly measures three aluminium fractions in waters: acid reactive aluminium (Al_r), total monomeric aluminium (Al_T) and non-labile monomeric aluminium (Al_n). From these three measurements, two more fractions can be calculated: "acid soluble" aluminium, from Al_r-Al_T, and "labile monomeric" aluminium (Al_l), from Al_T-Al_n. This Al_l fraction is the important one with regards to the toxicity of aluminium toward fish as it contains altogether the "free" aluminium, sulphate, fluoride and hydroxy species [1].

In this paper we will present the comparison of the analytical performance of two fully described methods for the determination of the Al_l fraction, both developed around the Driscoll fractionation philosophy. The first is a variation of the most popular Driscoll method at the present time, based on the reagent Pyrocatechol Violet (PCV) [15–18]. The second is a new Flow-Injection Analysis system, based on the on-line post-column derivatization reaction of aluminium with the reagent 8-hydroxyquinoline-5-sulphonic acid (8-HQS) in a miceller medium followed by its fluorimetric detection [19].

EXPERIMENTAL

Containers

All reagents and water samples were stored in high density polyethylene containers, previously leached with 10% nitric acid for 48 h, and filled with high purity water until use.

Water

High purity water (18 megohms) Milli-Q water was used throughout.

Reagents

General All reagents were supplied by E. Merck, Germany, and were of analytical grade unless stated otherwise.

—Aluminium standards were prepared from a 1000 μg l^{-1} stock solution. This was prepared by dissolving 1.000g of aluminium foil in 20 ml of 1+1 sulphuric acid and diluting to 1000 ml with ultrapure water and 50 ml of concentrated nitric acid.
—Concentrated Hydrochloric acid, Suprapure, as supplied.
—1.0 M stock solution of Sodium Chloride was prepared by dissolving 58.44 g of NaCl in water and making up to 1000 ml.
—Amberlite IR-120 P cation exchange resin (Sigma, St.Louis, MO, U.S.A.).

PCV Method

—0.0375 % m/v PCV solution.
—"Iron interference" solution containing 0.1% m/v 1,10 phenanthroline-monohydrate in a 10% m/v Hydroxylammonium chloride solution.
—Hexamine buffer containing 30% m/v Hexamethylenetetramine plus 1.6% v/v s.g. 0.88 ammonium solution (suprapure).

8-HQS Method

—The aluminium post-column derivatizing reagent contained 0.1216 g of 8-HQS (98%, Aldrich, Steinheim, Germany) and 0.3645 g Hexadecyltrimethylammonium bromide (CTAB) (98%, Fluka, Buchs, Switzerland) dissolved by sonication in a 250 ml plastic volumetric flask with 100 ml of a sodium acetate trihydrate buffer (85 g in 500 ml, adjusted to pH 6.0 with acetic acid), 62.5 ml of a 0.4% m/v 1,10 phenanthroline-monohydrate solution, and ultra pure water.

Instrumental

Spectrophotometric measurements for the PCV method were obtained with a Perkin-Elmer 124 double beam Spectrophotometer. 8-HQS fluorimetric measurements were taken from a Perkin-Elmer LS-3B Spectrofluorimeter containing a 12 μl flow cell. The signals from the fluorimeter were collected on a Shimadzu C-R3A Chromatopac digital integrator. A LKB 2150 LC pump was also used in the 8-HQS fluorimetric speciation method, a schematic diagram of which is given in Figure 1. A Conductivity meter Model 522 (Crison Instruments S.A, Barcelona, Spain) was used for the conductivity measurements and a Radiometer GK-2401-C combination glass-electrode for all pH determinations.

Samples

Lake water samples were collected from Lake Enol, Covadonga National Park, Asturias, Spain, and tap water samples from the domestic supply of the city of Oviedo, Asturias, Spain. All samples were collected in precleaned, high density polyethylene bottles and filtered through a 0.45 μm filter (Lida corp., Kenosha, WI, USA), and stored in the dark. Some sub-samples were spiked with various amounts of inorganic aluminium.

Procedures

As mentioned in the introduction, the Driscoll/PCV method is perhaps today's most widespread aluminium fractionation method. however, precise analytical details, and performance data, are few and far between, with various authors introducing modifications, but never publishing a definitive method. Here we present a PCV detection method in full, incorporating many published modifications which we considered enhanced the analytical performance of the whole method.

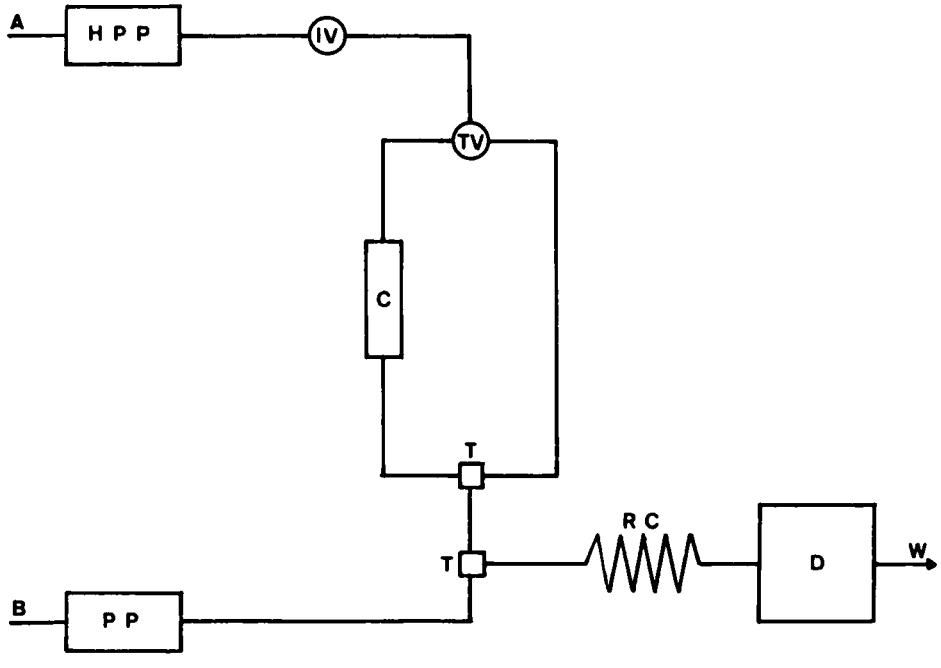

Figure 1 Schematic diagram of the Driscoll based 8-hydroxyquinoline-5-sulphonic acid FIA system. HPP= high pressure pump, IV=injection value, TW=two-way valve, C= ion-exchange column, D=fluorimetric detector, PP=peristaltic pump, W=waste, RC=2 m ×0.5 mm i.d. reaction coil, T=t-piece, A=NaCl eluent and B= post-column reagent.

Separation step: ion-exchange column

Two columns of Amberlite IR-120 cation exchange resin were prepared. One with an internal volume of 1 ml (0.4 cm × 8.0 cm) for the PCV colorimetric method and another with a internal volume of 0.35 ml (0.3 cm × 5.0 cm) for the 8-HQS fluorimetric method.

Column conditioning was performed as described by Driscoll [14], but from the Na^+ form and not from the H^+ form as originally specified. Once fabricated, the columns were cleaned with 3 ml of 1.0M HCl and then reconverted to the Na^+ form by passing a solution of 1.0M NaCl through them until the pH of the NaCl solution did not show significant change. The columns were then conditioned with a NaCl solution of the same ionic-strength as the water samples to be analyzed. The pH of the NaCl eluent solutions were not altered to that of the samples [14]. Trials have shown that this extra step is unnecessary to maintain the pH of the sample as it passed through the column and that the ionic strength of the NaCl solution is the critical factor. The column was considered conditioned when the pH of the effluent was within ± 0.2 units of the eluent pH [14].

The flow rates for the NaCl eluent and samples through the columns were as recommended by Driscoll [14] i.e. 3.5 ml min^{-1} per ml of resin bed.

PCV colorimetric detection of aluminium

General method 0.1 ml of "iron interference" solution and 0.2 ml of PCV reagent solution are added to 3.5 ml of the water sample. After vigorous mixing, 1.0 ml of the hexamine buffer is added. The absorbance, at 581 nm, of the resulting solution was read after 10 minutes ±10 s from the addition of the buffer. The reference cuvette contained water, and the zero absorbance was set with water in both the reference and sample cuvettes. The pH of the final solutions should be 6.1 ±0.1 pH units. Any deviations from this range will result in erroneous readings.

Acid reactive aluminium (Al_r) This fraction is determined as above but 25 µl of concentrated HCL is added to the 3.5 ml sample and left to react for one hour, before the addition of the PCV reagents.

Total monomeric aluminium (Al_T) No sample pretreatment is required for the determination of this fraction. However, 25 µl of concentrated HCl should be added *simultaneously* with the hexamine buffer. This is to ensure that the pH of the resulting solution is within the specified pH range of 6.1 ±0.1.

Non-labile monomeric aluminium (Al_n) Aliquots of sample are passed through the cation exchange column at a flow rate of 3.5 ml min^{-1}. The first 10 ml of exchanged sample is discarded, thereafter 3.5 ml fractions are collected and analyzed as for the Al_T fraction.

8-HQS fluorimetric detection method

Using the flow injection analysis (FIA) system shown in Figure 1, with a post-column

Table 1 Comparison of the analytical characteristics of the Pyrocatechol Violet (PCV) and 8-Hydroxyquinoline-5-sulphonic acid (8-HQS) aluminium detection methods.

Analytical Characteristic	*PCV*	*8-HQS*
System type	Batch	FIA
Detection	Spectrophotometric $\lambda = 581$ nm	Fluorimetric $\lambda_{ex} = 390$ nm $\lambda_{em} = 500$ nm
Reagants	Pyrocatechol Violet 1,10 phenathroline/ hydroxylammonium chloride	8-hydroxyquinoline-5-sulphonic acid/CTAB 1,10 phenathroline
Routine limit of detection	5–10 $\mu g\ l^{-1}$	$<1\ \mu g\ l^{-1}$
Dynamic Linear Range	20–400 $\mu g\ l^{-1}$	1–10,000 $\mu g\ l^{-1}$
Typical precision at 50 $\mu g\ l^{-1}$	4.3 %	1.4 % (peak height)
Sample volume Al_T	3.5 ml 15 ml	100 µl
Al_n	15 ml	100 µl
Speed of Analysis	10 min	20 s
Column Size	0.4cm × 8.0 cm	0.3cm × 5.0cm

reagent flow of 0.45 ml min^{-1} and a carrier sodium chloride flow of 1.0 ml min^{-1} (see Figure 1), 100 µl of untreated sample was injected into the system and two different peak height measurements were taken. The first from an injection of sample that by-passed the analytical column (the Al_T fraction) and the second from another injection of sample which passes through the column (the Al_n fraction). See Figure 1 for further details. The al_l fraction is taken to be the difference between Al_T and Al_n.

Table 1 gives a comparison of the major analytical features of the two detection methods used in this paper: PCV and 8-HQS, as experienced in our laboratory.

RESULTS AND DISCUSSION

PCV method

As mentioned in the introduction, the PCV method described here has been developed incorporating many features reported individually by other workers.

The concentrations of the reagents were taken directly from the original work of Dougan and Wilson [20]. Workers in recent years have tended to reduce the sample volumes from the original 35 ml [20] to 7 ml [18] or even to 3.5 ml [17]. This last volume was the one that we found to be the most convenient and satisfactory for the PCV procedure.

We also looked at the ion-exchange column size. In one of his first papers, Driscoll [14] specified a column of 1 cm in diameter, which contained 9.5 ml of prepared resin. With this column, and his recommended NaCl flow rate of 3.5 ml min^{-1} per ml of resin bed, impractical flows rates are required. Therefore the use of smaller columns have been reported and our 1 ml volume column size has also been reported by several groups [17, 21, 22].

This smaller size also helped in reducing the column conditioning time. Driscoll [14],

initially recommended conditioning the column from the H^+ form. This we found to be painstaking time consuming, specially with the very dilute NaCl eluents used. Therefore we developed the technique as described in Procedures, i.e. the column is initially cleaned with 1.0 M HCl, then converted to the Na^+ form and finally conditioned with a solution of NaCl of the correct ionic strength. We found that this procedure reduced the column conditioning time to 20–30 minutes.

A 10 minute reaction time of samples with the PCV reagent at the recommended pH of 6.1 was chosen [18, 20]. This factor did not seem to be very critical as several authors have reported minimal differences in results when using reaction times of between 4–20 minutes [16, 18].

A split calibration procedure was used for the PCV method. Using two calibration curves, one from 0–100 μg l^{-1} and the other from 100–400 μg l^{-1} [21] improved the accuracy of measurements, particularly of those samples containing less than 50 μg l^{-1} of aluminium.

8-HQS method

Based as the method above, around the Driscoll separation mechanism, we have developed a FIA system, coupled to a fluorimetric aluminium determination previously described by Garcia Alonso *et al.*[19]. The precedent for using 8-HQS for aluminium speciation analysis has already been set as the parent reagent, 8-hydroxyquinoline, was proposed for the measurement of rapidly reactive aluminium species [12,23], as well as its derivative 8-hydroxy-7-iodoquinoline-5-sulphonic acid (ferron) [1, 16].

The use of 8-HQS in a micellar medium, in this case CTAB, for aluminium derivatization has proven to be highly sensitive for aluminium, enabling 100 μl samples to be used in the FIA system shown in Figure 1. The use of a 2 m × 0.5 mm i.d. reaction coil, with the flow rates specified above, gives a reaction time between the sample and the post-column reagent of approximately 10–15 seconds. This is in-line with other workers using the derivatives of the same complexing reagent, when measuring the rapidly reacting or labile monomeric aluminium fraction in waters in batch systems [1, 23].

One of the major problems of the original fluorimetric method, however, was that Zn seriously interferred with aluminium analysis e.g. 100 μg l^{-1} Zn gave a signal enhancement of 200% in the analysis of 10 μg l^{-1} Al [19]. Therefore the system in the original form would not have been suitable for the Driscoll ion-exchange speciation method because Zn, if present in the sample, would be measured, along with the aluminium. Thus, Zn would be included in the Al_T fraction, but after passing through the column it would be retained and so absent for the Al_n measurement. This would give a positive bias to the calculated Al_l fraction.

To overcome this problem we added 1,10 phenathroline (to a concentration of 0.1% m/v) to the post column reagent). Typical Zn interference results for 20 μg l^{-1} Al solutions in our FIA system (Figure 1) are shown in Figure 2, for both detection with and without 1,10 phenathroline added to the post-column reagent. It can be clearly seen that for this aluminium concentration at least 150 μg l^{-1} of Zn can be tolerated by the fluorescence detection system. Further interference data is given in Table 2, where the improved post-column reagent system is compared to the data reported in an earlier paper [19]. A slight drawback of the 1,10

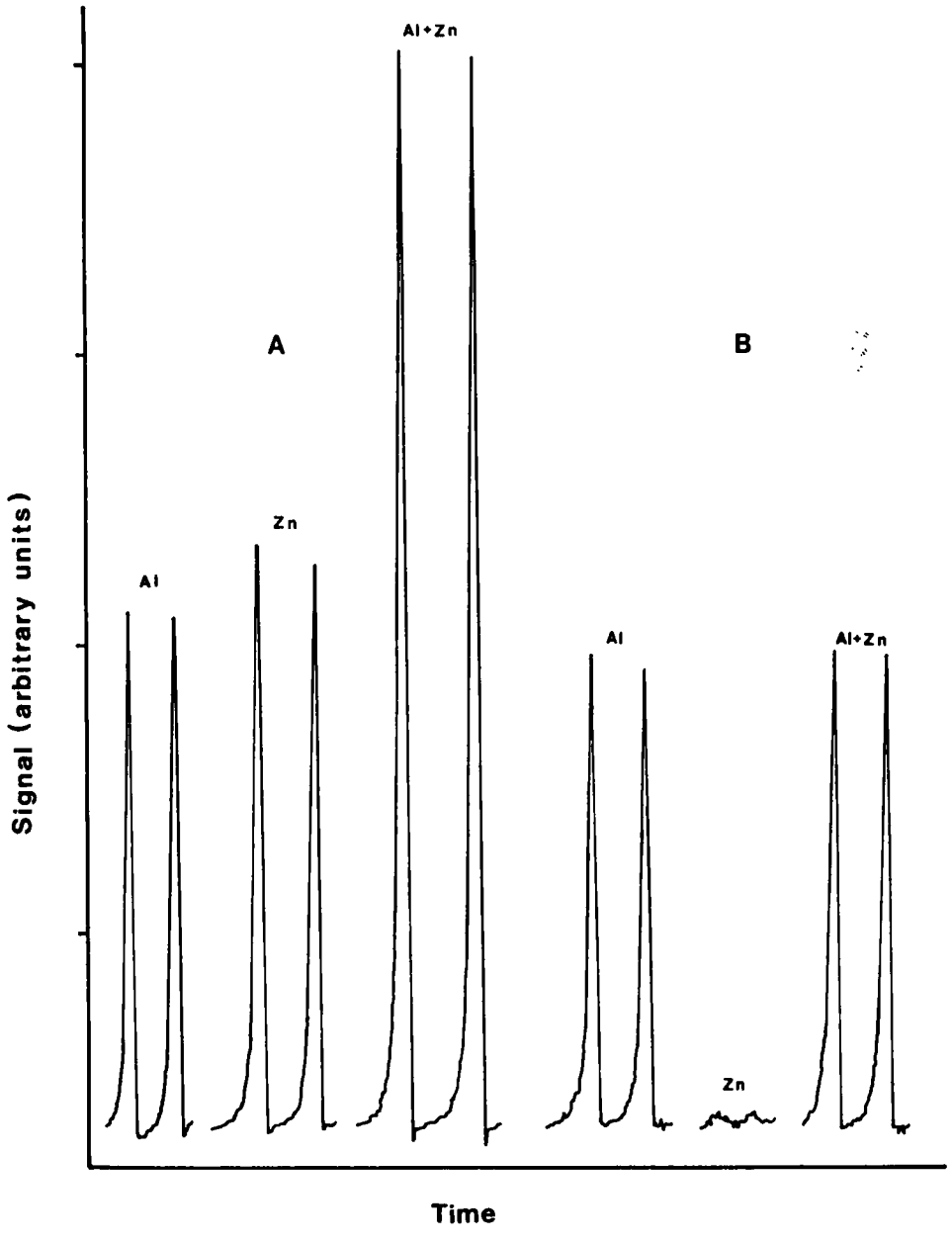

Figure 2 Analytical peaks demonstrating the interference caused by 150 μg l^{-1} Zinc on the signal for 20 μg l^{-1} aluminium as detected by the 8-HQS system. A) post-column reagent without 1,10 phenanthroline and B) post-column reagent with 0.1% m/v 1,10 phenanthroline.

Table 2 Interference levels tolerated by the FIA-8-HQS detection system for some common metals found in waters (Al concentration 20 μg l^{-1})

Element	*Maximum tolerated Concentration mg l^{-1} without 0.1% m/v* 1,10 Phenathroline*	*with 0.1% m/v$ 1,10 Phenathroline*
Zn	0.01	0.2
Fe	0.2	1.0
Cu	0.5	20
Mg	5.0	5.0

* reference [19] ± 10% error allowed
$ ± 10% error allowed

phenanthroline addition to the post-column reagents is that, as seen in Figure 2, there is a 8% loss in sensitivity when compared to the normal 8-HQS post-column reagent. However, this does not pose too much of a problem as the detection limit of the new system (0.9 μg l^{-1}) is still far superior than that of the batch PCV method.

Comparison of both Al speciation methods

As shown in Table 1, the FIA-8-HQS fluorimetric detection method has superior analytical characteristics than those of the conventional batch PCV colorimetric technique. The most striking features include the lower detection limit (which is especially important in water samples with a low total or organic aluminium content), the better precision (as the Driscoll

Table 3 Comparison of Driscoll/PCV and 8-HQS methods for the determination of the Al_I fraction for lake and tap waters. A=original lake water, B=lake water plus Al spike, and C=tap water plus Al spike.

Water sample	*PCV Method Al μg l^{-1}*	*8-HQS method Al μg l^{-1}*
A	NC	9.0 ± 3.4%
	NC	6.7 ± 1.6%
	NC	7.2 ± 7.8%
	NC	8.9 ± 7.8%
B	38.8 ± 5.2%	47.2 ± 1.1%
	40.2 ± 7.2%	47.7 ± 2.0%
	36.4 ± 5.9%	45.4 ± 1.8%
	34.6 ± 7.9%	46.3 ± 3.9%
C	ND	86.6 ± 0.7%
	83.2 ± 3.1%	90.1 ± 1.3%
	82.7 ± 4.3%	82.1 ± 1.0%
	87.4 ± 8.0%	75.9 ± 1.0%*

NC = not calculable.
ND = not determined
* = low Al_T result

method is a subtraction technique, the errors of the calculated Al_i fraction can sometimes become unacceptable with the PCV detection method [24]) and the reduction in analysis time/sample size needed for the FIA method. This reduction could be important as aluminium speciation analysis moves away from the research laboratories and becomes one of the routine analyses performed as an indication of water quality.

In order to validate the FIA-8-HQS method proposed here, a comparison of the two methods in the determination of the toxicologically important Al_i fraction was performed on Lake and Tap water samples. Three different types of samples were analyzed 4 times, over a period of 6 months. The original lake water contained a total aluminium concentration of 26.2 ± 1.2 μg l^{-1}. This low total aluminium content accounts for the series of "not-calculable" results shown in Table 3 for the PCV method, as many measurements of either the Al_T or Al_n fractions were below the detection limit of the technique. From Table 3 it can be seen that the two methods showed acceptable agreement for the Al_i fraction in the waters where there are positive results for comparison.

CONCLUSIONS

A FIA-fluorimetric method with improved analytical performance over the standard Driscoll/PCV method for the speciation of aluminium in waters is reported. The method, based on a FIA configuration, coupled to the fluorometric detection of the aluminium-8 hydroxyquinoline-5-sulphonic acid complex in a micellar medium, is superior to the batch Driscoll/PCV technique, in terms of precision, detection limit, analysis time, sample size and column characteristics.

Good agreement between the results observed by using the two methods for the determination of the Al_i fraction for a series of water samples over a period of 6 months was obtained.

A serious Al interference from Zn for the 8-HQS method, as reported for dialysis fluid analysis [19], has been overcome here by the addition of 0.1% 1,10 phenathroline to the post-column Al derivatizing reagent.

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