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Comparison of fluorimetric and inductively coupled plasma mass spectrometry detection systems for the determination of aluminium species in waters by high-performance liquid chromatography

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The comparison of element-specific detection using HPLC–ICP-MS with an established HPLC–fluorimetric method for aluminium speciation in waters is described. This comparison allowed the identification of some problems with a fluorimetric detection method based around 8-hydroxyquinoline-5-sulfonic acid, particularly its comparatively poor selectivity and Al-species dependent response factors. The power of ICP-MS as a detector for HPLC systems is demonstrated by the simultaneous detection of Al, Mg, Zn, and Fe. The increased selectivity of ICP-MS over molecular fluorescence is shown in the reliable quantification of Al^{3+} and AlF^{2+} in a range of tap and natural water samples. The fluorimetric technique exhibited varying response factors to different aluminium species while the specific detector gave constant signals. Both techniques provided similar values for the 'free' Al^{3+} fraction in a variety of natural waters but systematic differences were obtained in the quantification of the AlF^{2+} fraction. Problems with the ICP-MS detection method for Al-speciation analysis such as ion interferences and salt concentration of the mobile phase are commented upon.

Keywords: *Aluminium speciation; high-performance liquid chromatography; fluorescence; inductively coupled plasma mass spectrometry; waters*

The determination of aluminium species has been of interest to scientists since the recognition that certain Al-species are toxic to a variety of living organisms. In the environment, with the manifestation of the acid rain phenomenon, the mobilisation of Al from poorly buffered soils into the aquatic environment has been linked to the sharp decline in fresh fish population of several countries.[1] Aluminium has been shown to be phytotoxic,[2] and, under special circumstances, accumulation in humans can cause several unpleasant degenerative diseases such as dialysis dementia.[3] For fish populations the most toxic forms of Al have been found to be the most labile monomeric inorganic species such as $Al(OH)^{2+}$ and $Al(OH)_2^+$.[1] Depending on the local environmental conditions (*e.g.*, pH and $[Ca^{2+}]$), these species are thought to have a variety of toxicological actions such as simple clogging of the gills at higher concentrations, to disturbing the osmoregulatory balance in the fish's plasma[4] at the low μg dm^{-3} level.

However, one factor which dominates the analysis of aluminium species in natural water samples is that practically all of the analytical methodologies measure operationally defined fractions. These operationally defined protocols have been categorised by several workers, usually giving rise to the grouping of different methodologies under such titles as 'reaction rate' or 'size-exclusion' *etc*.[5,6] In many of these operationally defined fractionation methods, *e.g.*, the Driscoll/PCV method,[7] the chosen method of detection is an integral part of the speciation process. Many of these methods have unsatisfactory detection performance especially with regard to the levels of aluminium in environmental samples (low μg dm^{-3}).

During the last few years, high performance liquid chromatography (HPLC) has attracted the attention of several workers who have studied its potential for aluminium species analysis.[8–10] This analytical technique has several potential advantages over other speciation methods. The most important one is that it is not such an operationally defined method. Of particular interest is whether there is a rearrangement of aluminium species during the separation process. Bertsch and Anderson[9] and Motellier and Pitsch[10] performed detailed studies of the fluoro and hydroxy species of aluminium separated under a range of conditions, and found that the measured ratios agreed well with those calculated using thermodynamic data. Thus, the technique has the potential for the simultaneous determination of the Al–organic, Al–fluoride, and Al^{3+} (or inorganic monomeric) species in natural water samples. The other main advantage of these HPLC methods is that the separation process is independent from the detection, thereby allowing optimisation of the final measurement.

Recently, the use of 4,5-dihydroxy-1,3-benzenedisulfonic acid (Tiron) as an ultraviolet spectrophotometric post-column reagent for the detection of aluminium species in HPLC systems has been reported.[9–11] However, this detection method suffers from a lack of sensitivity, with quoted detection limits for the HPLC determination of Al^{3+} ranging between 7,[11] 10[9] and 20[10] μg dm^{-3}. These values are not quite sufficient for the precise and accurate quantification of Al species at environmental and toxicological levels. To overcome this problem Jones and coworker developed a HPLC method with fluorimetric post-column detection of Al species using 8-hydroxyquinoline-5-sulfonic acid (8-HQS). This method gave a detection limit for Al^{3+} of 1 μg dm^{-3} which enabled these workers to quantify the Al species in a range of natural and potable waters.[12,13] This fluorimetric detection method has several potential problems for the analysis of complex natural samples including varying response factors for different Al-species–fluorimetric reagent complexes, and possible important interferences from magnesium and zinc. The varying response factors for Al–fluoro species were overcome by injecting known mixtures of Al and fluoride. However, overlap with organo-aluminium and possibly magnesium peaks would lower the accuracy of the measurement.

This paper describes the coupling of an element specific detection method, of adequate sensitivity, in the form of

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inductively coupled plasma mass spectrometry (ICP-MS), to an established HPLC aluminium speciation procedure and compares its detection characteristics with those of a 8-hydroxyquinoline-5-sulfonic acid fluorimetric post-column detection method. The potential of using atomic spectrometric detection to solve several detection problems encountered with the HPLC–fluorimetric detection speciation method is discussed.

Experimental

Reagents

All reagents were obtained from Merck (Poole, Dorset, UK) or Sigma (Poole, Dorset, UK) and were of analytical-reagent grade or better. All solutions were prepared with high purity water (18 MΩ, Millipore, Watford, Herts, UK). An aluminium stock standard solution was prepared from high purity metal dissolved with H_2SO_4/HNO_3.[14] All reagents, standards and samples were stored in high density polyethylene containers, previously leached with 10% (v/v) HNO_3 for 48 h, and filled with high-purity water until use.[14] Humic acid (HA) was obtained from Fluka (Buchs, Switzerland). All synthetic standard mixtures containing Al, F^- or HA, were left for at least 24 h to stabilise before analysis.

Samples

All samples were taken in the area of Dartmoor National Park, UK. Tap water samples were taken from continuously running taps in Princetown. The moorland bog and moorland spring water samples were taken from the area around Princetown. The reservoir water was taken from Burrator reservoir, the catchment for which is Dartmoor National Park. Samples were collected in acid leached high density polyethylene containers (as above), and analysed as soon as possible for total Al content by inductively coupled plasma atomic emission spectrometry (ICP-AES). The speciation or distribution of the Al species present was carried out using the HPLC–fluorimetry and ICP-MS methods as soon as possible on return to the laboratory.

Instrumental

Two PU4010 (Unicam, Cambridge, UK) high pressure pumps were used for the HPLC–fluorimetric detection method. The instrument set-up is shown in Fig. 1. All fluorimetric measurements were obtained using a LS4 Fluorescence Spectrometer fitted with a 12 μl flow cell (Perkin-Elmer, Beaconsfield, UK) with data acquisition by a Nelson signal integrator system (Perkin-Elmer). The ICP-MS detection system was a VG PQ2+ instrument (VG Elemental, Winsford, UK). When coupled to the ICP-MS the HPLC system utilised a single, all titanium, LKB Bromma 2150 HPLC pump (Bromma, Cambridge, UK). All pH measurements were made using a model pHA-260 pH meter (Whatman, Maidstone, UK). For total Al determinations, a Liberty 200 (Varian, UK) ICP-AES coupled to a Liberty Star data acquisition workstation was used.

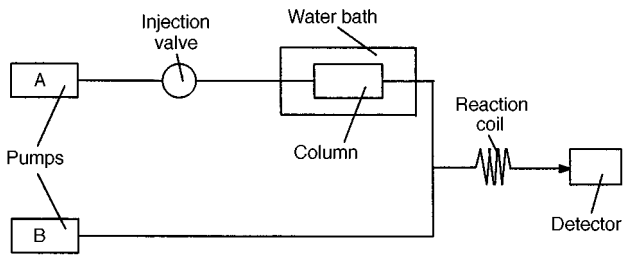

Fig. 1 Schematic diagram of the HPLC aluminium speciation system as set-up for fluorimetric detection. A, mobile phase pump; B, post-column reagent pump. For ICP-MS detection pump B and the reaction coil were not used.

Procedure

The ion chromatography method has already been published in full elsewhere.[12] It is based on a short (50 mm), low capacity cation-exchange column (Dionex CG2), with 0.08 M K_2SO_4 (0.75 ml min^{-1}) adjusted to pH 3.0 as the eluent. A 100 μl sample loop was used. Detection was achieved by either on-line post-column derivatization with a solution of 8-hydroxyquinoline-5-sulfonic acid (8-HQS; 0.002 M in 0.01 M NaAc/HAc buffer, pH 4.1, 1 ml min^{-1}) with continuous fluorescence monitoring (λ_{ex} 360 nm and λ_{em} 512 nm) or by ICP-MS. Normal ICP-MS operating conditions for Al detection are given in Table 1. In the HPLC separation the 'labile monomeric' inorganic Al species (except the $[AlF_n]^{(3-n)+}$ species which are excluded from the measured fraction) are all converted to Al^{3+} at pH 3.0 and are eluted together. This peak, which is usually $Al(OH)_n^{(3-n)+}$ where *n* varies between 0 to 4, is called the 'Al^{3+} peak' and it is an estimation of the toxic Al fraction. Peak area measurements were used for quantification purposes. All subsequent data handling was performed off-line using standard PC graphical and statistical software.

Results and discussion

Fluorimetric detection method

A typical chromatogram of a moorland bog water (original pH 5.2), obtained using the system shown in Fig. 1 with fluorescence detection, is presented along with chromatograms of standard solutions in Figs. 2(*a-c*). To study the possible identification and quantification of all the peaks obtained, the ionic strength of the mobile phase was optimised for the separation of the peaks coming out near the solvent front. If only the Al^{3+} fraction is to be determined, a stronger ionic strength mobile phase can be used and the Al^{3+} peak can be base-line resolved from the other peaks within 3.5 min.[12] Using the experimental conditions described above several problems can be clearly identified from Fig. 2(*a*) if all the peaks corresponding to other Al species present in the sample are to be quantified.

Interferences

It is evident from Fig. 2(*a*) that at least three poorly resolved species eluted within approximately 120 s, and a further well resolved peak after 360 s. Each peak in Fig. 2(*a*) was tentatively

Table 1 ICP-MS operating conditions

Model	VG PQ2+ (Fisons)
Ion masses (*m/z*)	$^{27}Al^+$, $^{24}Mg^+$, $^{68}Zn^+$, $^{58}Fe^+$
Forward power	1.35 kW
Carrier gas	16.5 l min^{-1}
Auxillary gas	0.8 l min^{-1}
Nebulizer gas	0.8 l min^{-1}
Sampling depth	10 mm
Sample flow	1.0 ml min^{-1}
Data acquisition	Time resolved mode
Points per peak	3
DAC step	5
Dwell time	52 ms
Time-slice duration	1 s
Interface	High performance
Sampler	Ni, 1.0 mm Ø orifice
Skimmer	Ni, 0.7 mm Ø orifice
Torch	Fassel (quartz)
Nebulizer	V-groove high solids

identified by injections of the appropriate single standard solutions, as shown in Figs. 2(*b*) and 2(*c*), and by comparison of retention times shown in Table 2. It is probable that the first peak in Fig. 2(*a*) was 'organic Al' species (*c.f.*, Table 2). The retention time was not the same as the standard Al–HA species [peak A in Fig. 2(*b*)], but this is not surprising because it is impossible to obtain synthetic humic acid which is exactly the same as the natural form, and there may be a range of organic ligands complexing with Al in the sample. The second peak in Fig. 2(*a*) was probably AlF^{2+} [*c.f.* Table 2 and peak B in Fig. 2(*b*)], the third peak was probably Zn^{2+}, Mg^{2+} or another M^{2+} ion [*c.f.*, Table 2 and peak C in Fig. 2(*c*)], and the fourth peak was Al^{3+} [*c.f.*, Table 2 and peak D in Fig. 2(*b*)].

It is apparent that the quantification of the first three peaks in Fig. 2(*a*) was difficult because of the poor chromatographic resolution. The AlF^{2+} peak was on the shoulder of the 'organic Al' peak which arises from the complexation of any Al, Fe, Mg or Zn bound-up with the dissolved organic fraction of the sample. Secondly, both Mg and Zn eluted just after the AlF^{2+} peak [Fig. 2(*c*)] compounding the tailing effect from the 'organic-Al' peak. The severity of this latter effect is dependent on which M^{2+} species are present because, for example, Zn^{2+} is very sensitive to this detection system whereas Mg^{2+} is much less so. Usually, it is necessary to carefully optimise the mobile phase ionic strength and post-column reagent pH to keep these interferences to a minimum.[13]

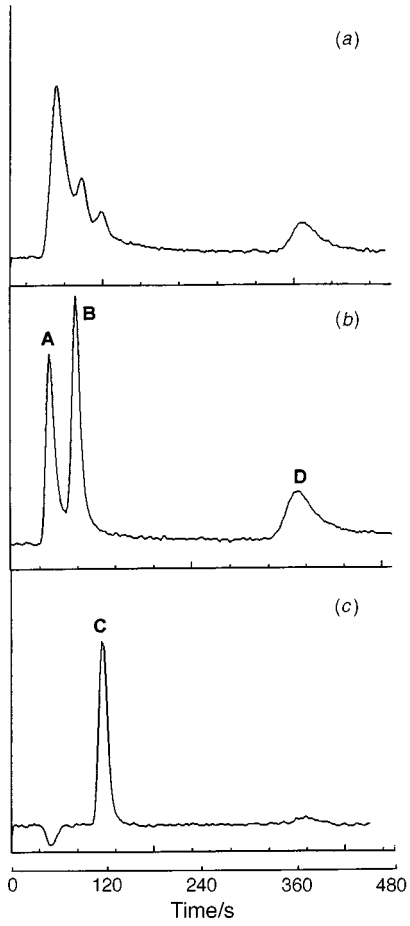

Fig. 2 Typical chromatograms obtained using fluorimetric detection. (*a*) Moorland bog water; (*b*) mixed standard of Al (200 μg dm^{-3}), F^- (30 μg dm^{-3}) and HA (10 mg dm^{-3}) pH 4.5; and (*c*) Zn (20 μg dm^{-3}). All chromatograms are in the same scale of 0–75 mV. Peak A, Al–organic; Peak B, AlF^{2+}; Peak C, Zn; and Peak D, Al^{3+}.

Table 2 Retention times and tentative identification of species determined by HPLC coupled with fluorimetric detection

Standard solution		Acidic moorland water	
Retention time/s	Species	Retention time/s	Possible species
48	Al-HA	58	Al-HA
84	Al-F^{2+}	91	Al-F^{2+}
115	Zn^{2+}	115	Zn^{2+}
360	Al^{3+}	360	Al^{3+}

Response factors

Ideally, detection systems should show the same response for equimolar amounts of Al atoms regardless of which Al-containing species is involved, *i.e.*, they should give the same integrated peak areas in the chromatogram. It has been reported that, with the use of Tiron for the spectrophotometric detection of Al^{3+} at 310 nm, the total integrated area is conserved between Al^{3+} and AlF^{2+} species in synthetic solutions, indicating the complete dissociation of the Al–fluoride species and quantitative complexation of the resultant Al^{3+} cation.[9,10] This was tested for the 8-HQS detection system using standard solutions of mixtures of Al and fluoride, prepared at pH 3.0 and left for 24 h before analysis by the HPLC–fluorimetric method. The results are given in Table 3 and clearly show that for this simple two-species system the total integrated area was not conserved. The AlF^{2+} species was found to have a response factor (*i.e.*, units of integrated area per unit of Al concentration) of nearly three times that of the Al^{3+} ion.

ICP-MS detection

The moorland bog water was re-analysed using HPLC coupled with ICP-MS detection, and typical chromatograms obtained are shown in Fig. 3. The ICP-MS was set-up to monitor the $^{27}Al^+$, $^{24}Mg^+$, $^{68}Zn^+$ and $^{58}Fe^+$ isotopes simultaneously. Exactly the same chromatographic conditions were used as for the fluorimetric detection experiments, however, the retention times were slightly longer because it was necessary to use a pump rate of 0.5 ml min^{-1}. Retention times for the individual Al species are shown in Table 4.

The advantages of ICP-MS as an element-specific detector for the HPLC system are immediately apparent. The instrument used in this work has a quoted detection limit for Al of 0.1 μg dm^{-3}[15] which puts it on a par with the fluorimetric detection method for Al[12] and therefore suitable for this type of analysis. However, the main advantage of this technique is the unequivocal nature of the element-specific detection, which makes it possible to resolve interferences that cannot be resolved by a non-specific detection method such as fluorimetry.

Interferences

The ion masses monitored were dictated by isotopic overlap and by possible polyatomic ion interferences. In the case of Zn it was necessary to use the third most abundant isotope, ^{68}Zn,

Table 3 Response factors for various aluminium species to the fluorimetric 8-hydroxyquinoline-5-sulfonic acid detection system

Solution	Species	[Al] in peak/ μg dm^{-3}	Peak area/ mV × 10^4	Response factor
1	Al^{3+}	200	87.5	1.00
	AlF^{2+}	0	0	0.00
2	Al^{3+}	173	73.4	0.97
	AlF^{2+}	27	40.1	3.39
3	Al^{3+}	146	65.1	1.02
	AlF^{2+}	54	78.5	3.32

because ^{64}Zn and ^{66}Zn could have been subject to possible polyatomic interferences at *m/z* 64 and 66 due to S_2^+ and SO_2^+, respectively, formed from constituents in the mobile phase.[16] It is also possible that $^{27}Al^+$ may suffer from interferences due to $^{13}C^{14}N^+$ and $^{12}C^{14}NH^+$, particularly in the presence of humic complexes, though the concentration would have to be extremely high to cause significant interference. However, provided such precautions are taken, the detection method should result in unequivocal identification and quantification of the metal moiety in the species studied. Fig. 3 is comprised of four chromatographs for moorland bog water, obtained simultaneously at the four masses studied. Fig. 3(*a*) shows the chromatograph obtained for *m/z* 27 (*i.e.*, Al detection) and clearly shows that Al was associated with the first two, unresolved peaks ('organic Al', AlF^{2+}), and the fourth well resolved peak (Al^{3+}), observed using fluorimetric detection [*c.f.*, Fig. 2(*a*)], but the third unresolved peak was absent or at least much diminished. The Mg-, Zn-, and Fe-containing species were resolved from the Al-containing species by the element-selective nature of the detection, and were identified and quantified using the element-selective chromatographs for Al, Mg, Zn, and Fe shown in Fig. 3, and are summarised in Table 4. Fig. 4 shows the chromatogram obtained for the mixed standard of Al with element-selective detection at *m/z* 27 for Al, hence allowing the Al containing fractions to be tentatively identified, as listed in Table 4.

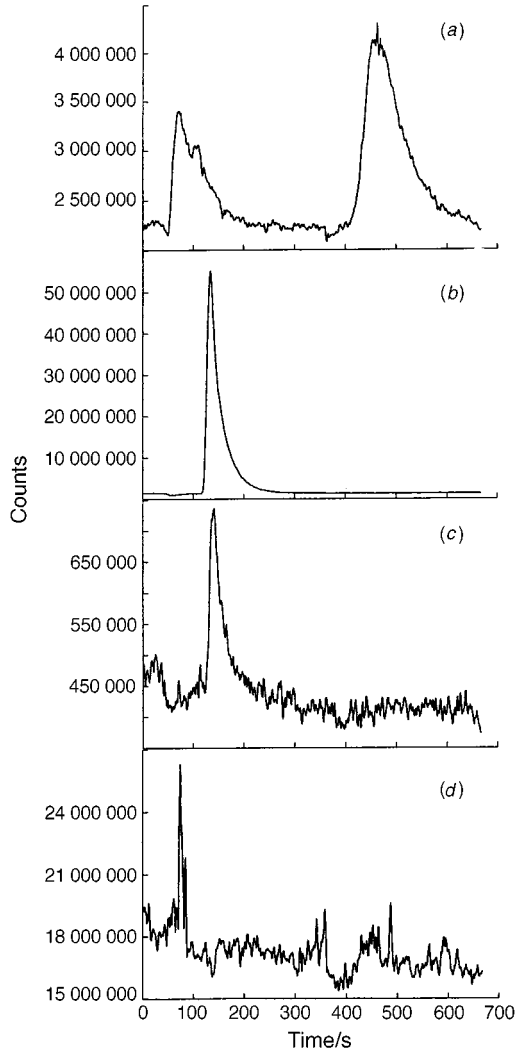

Fig. 3 Chromatograms for the moorland bog water, obtained using ICP-MS detection and simultaneous multi-isotopic monitoring at: (*a*) *m/z* 27 for Al; (*b*) *m/z* 24 for Mg; (*c*) *m/z* 68 for Zn; and (*d*) *m/z* 58 for Fe.

Table 4 Retention times and tentative identification of species determined by HPLC coupled with ICP-MS detection

Standard solution		Acidic moorland water	
Retention time/s	Species	Retention time/s	Possible species
63	Al-HA	72	Al-HA
107	Al-F^{2+}	105	Al-F^{2+}
-	-	135	Mg^{2+}
-	-	139	Zn^{2+}
467	Al^{3+}	462	Al^{3+}

A semi-quantitative analysis of the moorland bog water by ICP-MS provided values of 2 mg dm^{-3} and 15 μg dm^{-3} for Mg and Zn respectively. It was not possible to detect Mg^{2+} at this concentration using the fluorimetric detection method, so no interference due to Mg^{2+} was observed using this method, however, a considerable interference from Zn would be expected, as shown in Fig. 2(*a*) and 2(*c*). Also, the element-selective chromatograph for Fe [Fig. 3(*d*)] revealed that there was some Fe associated with the organic matter in the sample, which could result in a possible interference on the 'organic-Al' peak [the first peak in Fig. 2(*a*)] due if fluorimetric detection was used.

Response factors

With ICP-MS detection, all of the aluminium-containing fractions produced by the HPLC separation should give the same response at the detector, assuming that the transport and nebulization processes for each Al species are equal. This is illustrated in Fig. 4, which is a chromatogram of the same mixed standard shown in Fig. 2(*b*), but obtained with ICP-MS detection and element-selective detection at *m/z* 27 for Al only. In this case ICP-MS was no more sensitive than fluorimetric detection, and detection limits were poorer due to the high Al background. Also, it was equally sensitive for all three Al species, was more sensitive for Mg, and less sensitive for Zn. The ICP-MS technique should yield equal response factors for equal concentration of the Al moiety. The total peak area for the three species (Fig. 4) was 95% of the peak area obtained for an injection of 200 μg dm^{-3} Al^{3+} standard which, while not conclusive, is some evidence that equal responses were indeed observed using ICP-MS detection.

Problems

The only real problem encountered with coupling ICP-MS to the HPLC system used in this study was the high salt content of the mobile phase. Curiously, this was not found to be a major problem for the cones in the interface between the ICP source

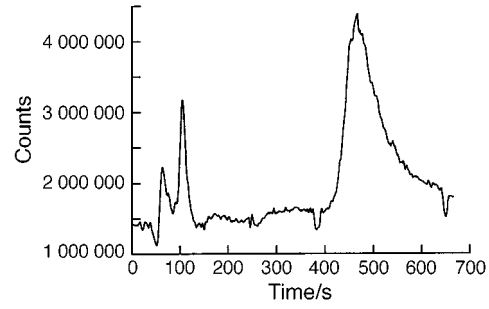

Fig. 4 Chromatogram of a mixed standard of Al (200 μg dm^{-3}), F^- (30 μg dm^{-3}) and HA (10 mg dm^{-3}) at pH 4.5, obtained using ICP-MS detection at *m/z* 27 for Al.

and the MS detection unit, but for the injector tube inside the ICP torch. Care had to be taken that an unrestricted injector tube was used, as salt deposits built up extremely quickly if the injector tube had a restriction neck. Even so, with a straight injector tube, the ICP-MS could only be run for 2 h at a time before salt build-up became a problem. The use of other mobile phases such as NH_4Cl–HCl[10] or $(NH_4)_2SO_4$,[11] which have been used with the type of HPLC column used here, may overcome this problem.

Analysis of water samples

A final comparison between the two detection techniques consisted of the determination of both the AlF^{2+} and Al^{3+} concentrations in a variety of moorland and tap water samples. Calibration was performed using mixed species standards for the fluorimetric method, and the use of single Al^{3+} standards, which were eluted through the column, for the ICP-MS analysis, given that the response factors were the same for all three species using ICP-MS detection. The results obtained using both fluorimetric and ICP-MS detection are given in Table 5, and the sum of the AlF^{2+} and Al^{3+} is compared with the total Al, determined by ICP-AES, in Table 6. As can be seen, for the determination of the Al^{3+} fraction, both detection techniques gave similar results within the error limits. However, for the tap water sample the fluorimetric method yielded a higher result for Al^{3+} (Table 5), and the sum of Al^{3+} + AlF^{2+} exceeded the total Al determined by ICP-AES (Table 6) by 15%. The fluorimetric detection method also consistently gave higher values for the AlF^{2+} fraction regardless of sample type (between 27–300% higher). Possible reasons for this could be the poor resolution between the 'organic Al' and AlF^{2+} species, possible interferences due to Zn and Mg, or the presence of unidentified, unresolved species. Poor resolution between the AlF^{2+} and 'organic Al' peaks was a major problem only for the moorland bog water sample [Figs. 2(*a*) and 3(*a*)], which contained a relatively large concentration of 'organic Al', whereas the other samples contained relatively little of this species. In general higher results were obtained for total Al, determined by ICP-AES, compared with the sum of Al^{3+} + AlF^{2+} species (Table 6), with the exception of the tap water using fluorimetric detection. It would be surprising if the sum of the species agreed with the total Al result because the 'organic Al' fraction has not been taken into account. The moorland bog water contained the highest concentration of 'organic Al' compared with the other species, hence the discrepancy between the sum and total Al in Table 6. The moorland spring contained relatively little 'organic Al', as did the reservoir water, and the tap water contained none. As can be seen from Table 6, the samples which contained the least 'organic Al' exhibited the best agreement between the sum of Al^{3+} + AlF^{2+} and total Al, as would be expected. Other reasons for the discrepancies may be that some Al species did not elute from the column, or were present at levels below the detection limit. Hence, it is impossible to draw firm conclusions from these results, other than the observation that ICP-MS may be less prone to interferences than fluorimetric detection, especially for the AlF^{2+} determination.

Table 5 Results of the analysis of moorland and tap waters for their Al^{3+} and AlF^{2+} concentrations by HPLC using fluorimetric and ICP-MS detection

		$[Al^{3+}]$ /μg dm^{-3}		$[AlF^{2+}]$/μg dm^{-3}	
Sample	pH	Fluorimetric	ICP-MS	Fluorimetric	ICP-MS
Reservoir	6.3	16.0 ± 3.1	14.9 ± 2.7	3.6 ± 2.2	1.8 ± 1.3
Moorland bog	5.2	30.8 ± 2.0	42.3 ± 4.6	4.8 ± 1.2	1.2 ± 0.8
Tap	8.7	207 ± 11	187 ± 13	23.6 ± 1.5	9.6 ± 2.0
Moorland spring	5.2	93.3 ± 5.1	92.3 ± 3.4	46.4 ± 1.5	36.5 ± 2.3

Table 6 Results of the analysis of moorland and tap waters for their total Al concentration determined by ICP-AES, compared with the the sum of Al^{3+} and AlF^{2+} concentrations determined by HPLC using fluorimetric and ICP-MS detection

		Sum of $[Al^{3+} + AlF^{2+}]$/μg dm^{-3}	
Sample	Total Al*/ μg dm^{-3}	Fluorimetric	ICP-MS
Reservoir	23.0 ± 1.2	19.6 ± 3.8	16.7 ± 3.0
Moorland bog	86.2 ± 2.4	35.6 ± 2.3	43.5 ± 4.7
Tap	201 ± 6	231 ± 11	197 ± 13
Moorland spring	155 ± 5	140 ± 5	129 ± 4

* Determined by ICP-AES.

Conclusion

Fluorimetric and ICP-MS detection systems have been successfully coupled to a HPLC system for the speciation of aluminium in water samples. Several advantages of the element-specific ICP-MS over the traditional fluorimetric detection system in the areas of calibration (*i.e.*, response factors) and in selectivity have been demonstrated. A range of natural waters were successfully analysed for their Al^{3+} and AlF^{2+} contents with both methods giving comparable results for the Al^{3+} fraction. Differences were found between the two methods for the quantification of the AlF^{2+} peak. Problems with high salt content in the ICP torch were identified.

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