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An automated method for monitoring aluminum in water samples based on a sequential injection platform

H. Sklenářová,*[a] B. Fialová,[a] J. Šandrejová,[ab] P. Chocholouš[a] and P. Solich[a]

The simple colour reaction between aluminum(III) and aluminon reagent was transferred to an automated sequential injection system. The experimental conditions were optimized in detail and found to be: sample pH, 4; zone sequence, aluminon–sample–HCl–aluminon; sample volume, 50 μL; volume of 1 M HCl, 5 μL; volume of reagent, 25 μL. The interference caused by iron was eliminated by the addition of thioglycolic acid. The calibration plot was linear over the range of 100–800 μg L^{-1} Al(III) with limits of detection and quantitation of 13.0 and 43.3 μg L^{-1}, respectively. The sample throughput was 36 samples per hour. The RSD values for repeatability tested on 200 and 600 μg L^{-1} Al(III) levels were found in the range of 1.97–2.36% and 1.69–2.57%, respectively. Nine real samples of well and pond water were examined and the results corresponded well with the commercially available colour test based on the chromazurol reaction. The recovery based on the standard addition method ranged from 100.00 to 103.41%. The developed method is intended to be applied for the quick screening of Al(III) content using a fully automated technique based on the sequential injection system.

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Introduction

The level of aluminum ions in different sample matrices was discussed frequently in the last years. The aim of the presented work is not based on the toxicological effects of aluminum on human health but on simple and quick fully automated aluminum ion determination in water samples. The automation of inorganic species determinations in water quality control was a quickly developing field for the last several decades. Flow techniques, mainly flow injection analysis (FIA) and sequential injection analysis (SIA), showed their advantages in terms of being fully automated systems, allowing quick analysis without the need to reach a steady-state reaction, decreased consumption of reagents and acceptable repeatability. And additionally flow systems could be used for different reasons not only for detection but also for sample pretreatment including preconcentration, separation or extraction procedures.

The transfer of simple but validated manual determinations to flow systems is relatively slow but some of them were mainly based on continuous flow analysis (CFA) and FIA, and were accepted by national authorities and even included into the European technical norms. The determination of nitrites and nitrates was the first water quality control method that could be carried out in both of the mentioned flow systems.[1] Methods for other analytes have followed: phenol index,[2] chlorides,[3] soluble silicates,[4] orthophosphates and total phosphorus,[5] ammonium nitrogen,[6] chromium(VI),[7] sulphates,[8] methylene blue active substances,[9] total nitrogen after UV digestion[10] and total and free cyanides.[11]

The practical advantages and drawbacks of sequential injection analysis compared to flow injection analysis were discussed in detail by the group of Cerda.[12] They mentioned robustness, easy sample handling, multi-parametric determinations, versatile manifold, easy implementation of stop-flow techniques and lower consumption of reagents and samples in the case of SIA determinations and also lower waste production. On the other hand the drawbacks could be found in the lower sample throughput that is based on the bi-directional movement of the piston pump in SIA compared to continuous flow in the FIA systems where more than one hundred samples per hour could be injected.

Concerning aluminum ions, determinations by many automated methods have been developed using different complex reactions and spectrophotometric or spectrofluorometric detection in the FIA or SIA system. Spectrophotometric determinations were based mainly on pyrocatechol violet, eriochrome cyanine and aluminon. The sensitivity and selectivity of these colour reactions are well known and were discussed with respect to their application in the flow injection system and the effect of different interference ions and their possible suppression.[13] Speciation of free aluminum ions and its hydroxo-complexes in the flow system was based on the reaction with a 8-quinolinol-derivatized Fractogel where a LOD of 70 nM

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[a] *Department of Analytical Chemistry, Faculty of Pharmacy, Charles University, Hradec Kralove, Czech Republic. E-mail: Hana.Sklenarova@faf.cuni.cz*

[b] *Department of Analytical Chemistry, University of P.J. Safarik, Kosice, Slovak Republic*

and a linear range of 0.3–16 μM were reached.[14] A flow injection system with spectrophotometric detection was developed for the determination of aluminum ions in hemodialysis solutions where a reaction with eriochrome cyanine was applied.[15] In this case recovery was the main evaluated parameter because of the sample matrix effect, and values in the range of 90.4–109% were found.

Nowadays many fluorometric determinations can be found in the literature. For example 8-hydroxyquinoline-5-sulfonic acid was used for the SIA determination with fluorometric detection of aluminum in drinking waters. This determination had: a linear range of 17.8–300 μg L^{-1}, a limit of quantitation (LOQ) of 18.1 μg L^{-1}, repeatability of 1.52%, a recovery for the real samples analysed of 92% and a sample throughput of 20 h^{-1}.[16] The same complex reagent was used in a time-based multisyringe FIA system where fluorescence detection was enhanced by micellar medium and thus: the linear range was broadened to 10–500 μg L^{-1}, the limit of detection (LOD) was 0.5 μg L^{-1}, and by parallel analysis of the 3 sample injections, a throughput of 154 h^{-1} was reached.[17] On-line monitoring of the aluminum content in drinking water with fluorometric detection based on the reaction with morin, with the LOD at 3.1 μg L^{-1}, linearity in the range of 2–250 μg L^{-1} and a sample throughput of 90 h^{-1} was also reported.[18]

Micellar media enhancement of the fluorescence signal was also applied for the SIA determination in drinking water based on the aluminum–morin complex. The mentioned reaction was linear in the range of 50–1000 μg L^{-1} with a LOD of 3 μg L^{-1} and acceptable recovery of 91–97%, and a sample throughput of 16 h^{-1}.[19] A derivative of quinoline sulfonic acid was also used in another work where a similar calibration range of 100–800 μg L^{-1} and LOD of 4 μg L^{-1} were obtained together with recovery of 92–101% and a sample throughput of 16 h^{-1}.[20]

A different reagent – *N*-*o*-vanillidine-2-amino-*p*-cresol – was tested in the FIA system where a similar linear range but a lower LOD (0.057 μg L^{-1}) were found.[21] Even a different flow injection strategy based on reverse FIA where the injection of the sample was replaced by the injection of the reagent to the sample stream was tested, a high sample throughput of 60 h^{-1} was found but there was lower sensitivity; the linear range was 20–500 μg L^{-1}, the LOD and LOQ were 7 and 24 μg L^{-1}, respectively.[22] Also a novel approach for magnetic stirring-assisted dispersive liquid–liquid microextraction was tested for aluminum determination.[23]

Outside the field of automated analytical techniques, spectrofluorometry was widely used for aluminum assays. To overcome the problems with high sample matrix effects, a separation/preconcentration method was recently described and used for aluminum determination in drinking water and biological samples (human hair).[24] A green preconcentration technique of dispersive liquid–liquid micro-extraction (DLLME) was combined with aluminum–morin complex formation followed by inductively coupled plasma-optical emission spectrometry (ICP-OES). In this case, solidification of a floating organic drop was applied with an enrichment factor of 128.[25] An ion-selective electrode was also used for aluminum determination in pharmaceutical substances, tea leaves and water samples.[26] And speciation of free aluminum and various aluminum fluoride complexes was accomplished by ion chromatography.[27] Another determination was based on the combination of liquid-based dispersive micro-extraction with stopped-flow spectrofluorometry which was applied for the determination of aluminum ions in natural waters, fruit juice and food samples.[28]

The recently published aluminum determination based on visual detection of the reaction product of aluminum ions with a cinnamoyl derivative, was optimized in the sequential injection system and applied for the determination in spiked water samples and pharmaceutical formulations.[29]

The possibilities of determination of aluminum in natural water samples were discussed in the terms of different detection techniques including atomic spectrometry, voltammetry, gas chromatography, spectrophotometry and fluorometry.[30] In the field of fluorometry, a summary of the common reagents is quercetin, morin, pyrocatechol violet, eriochrome cyanine, lumogallion, 8-hydroxyquinoline, salicyl-aldehyde-picolinoyl-hydrazone and chromotropic acid.

The proposed automated SIA method was based on the reaction with the specific complex reagent aluminon that is characterized by the quick formation of a red complex with aluminum ions at pH 4 (batch conditions). Following the technical norm (83 0520(22))[31] the absorbance is scanned after 15 min of heating and then cooling down to room temperature. But in our preliminary batch experiments the kinetics of this reaction was found to be fast enough for the transfer to the flow system. A simple and, after elimination of ferrous and ferric ions matrix effects, selective reaction for aluminum determination in surface water samples was described. The linear range, LOD, LOQ and sample throughput were mentioned together with previously published flow determinations based mainly on spectrophotometric and spectrofluorometric detections (summarized in Table 1). The proposed method was applied for the analysis of real surface water samples and the obtained results were compared to the simple aluminum colour test based on the chromazurol reaction. The comparison with such a simple method was selected because of the same analysis purpose – quick screening of water samples with respect to the accepted aluminum(III) concentration level in drinking water.

Experimental

Reagents

All chemicals were of analytical grade quality and ultra-pure water was produced by a Millipore Milli-Q RG system (Millipore, USA) and was used throughout the work. Aluminum chloride which was used as the aluminum ion standard was purchased from Lachema (Czech Republic). Aurintricarboxylic acid ammonium salt (aluminon) which was used as a reagent was obtained from Sigma-Aldrich (Czech Republic). Hydrochloric acid and ammonium acetate were supplied by Penta and Lachema (Czech Republic), respectively. Thioglycolic acid (99%) which was used to suppress the interfering effects of ferrous and ferric ions was obtained from Sigma-Aldrich (Czech Republic).

Table 1 Previously published spectrophotometric and spectrofluorometric determinations of aluminum ions in flow systems

Reagent	Linear range	LOD	LOQ	Sample throughput [h^{-1}]	Citation
8-Quinolinol	0.3–16 μM	70 nM			14
Eriochrome cyanine	10.8–650 μg L^{-1}	3.24 μg L^{-1}		30	15
8-Hydroxyquinoline-5-sulphonic acid	17.8–300 μg L^{-1}		18.1 μg L^{-1}	20[a]	16
8-Hydroxyquinoline-5-sulphonic acid	10–500 μg L^{-1}	0.5 μg L^{-1}		154	17
Morin	2–250 μg L^{-1}	3.1 μg L^{-1}		90	18
Morin	50–1000 ppb	3 ppb		11[a]	19
8-Hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulphonic acid	100–800 ppb	4 ppb		20[a]	20
N-*o*-Vanillidine-2-amino-*p*-cresol	Up to 1000 μg L^{-1}	0.057 μg L^{-1}		30	21
Quercetin	0.02–0.50 mg L^{-1}	0.007 mg L^{-1}	0.024 mg L^{-1}	60	22
Lumogallion	Up to 1.1 μM	6.1 nM		17	23
Morin	0–100 μg L^{-1}	0.24 μg L^{-1}			24
8-Hydroxyquinoline	0.06–15 μg L^{-1}	0.05 μg L^{-1}		40	28
Cinnamoyl derivative	55–660 μg L^{-1}	4 μg L^{-1}		16	29
Aluminon	**100–800 μg L^{-1}**	**13.0 μg L^{-1}**	**43.3 μg L^{-1}**	**36**	**Presented**

[a] Measured in triplicate.

Aluminum ion stock solution was prepared by dissolving aluminum chloride in water (100 mg L^{-1} of aluminum ions); the working solutions were diluted to obtain concentrations in the range of 20–1000 μg L^{-1} of aluminum ions. The reagent working solution was prepared by dissolving 0.09 g of aluminon in 10.00 mL of water, followed by mixing with a solution of 13.30 g of ammonium acetate in 10.00 mL of water and with 12.60 mL of 1 M HCl and filled up to 25 mL in a volumetric flask. Following the preparation procedure found in the technical standard (Technical norm 83 0520(22),[31]) only the higher concentration of reagent (3.6 g L^{-1} instead of 0.9 g L^{-1} of aluminon applied in batch conditions), that is commonly needed in the transfer of reactions from batch to flow conditions, where complete mixing is not achieved, was used. The pH value of the obtained solution was adjusted to 3.9 using acetic acid. Then solution stability for 6 months was guaranteed. A solution of thioglycolic acid (added to real samples) was prepared by dilution with water to get a 1% solution.

The colour test used for the comparison of the real sample determinations – aluminium test, Aquaquant – was obtained from Merck (Germany).

Apparatus

The setup corresponded to a commercially available FIAlab® 3000 system (FIAlab® Instrument Systems Inc., USA) with a syringe pump (syringe reservoir 5 mL), a central eight-port Cheminert selection valve and a 70 cm long PTFE tubing reaction coil (0.50 mm i.d.). The fiber-optic charge-coupled USB 2000 detector (Ocean Optics Inc., USA) equipped with a VIS light source LS-1 tungsten lamp (Ocean Optics Inc., USA) and a capillary Z-flow cell of 10 mm path length was used for detection. The latest version of the FIAlab® software (version 5.9.312) was employed for system control and data acquisition. The geometry of the SIA system is depicted in Fig. 1.

Batch experiments were carried out in test tubes and the absorbance was measured using a diode array spectrophotometer HP 8453 (Hewlett Packard, USA). A Sonorex RK 100 (Bandelin Electronic, Germany) ultrasonic bath was used for experimental conditions testing.

Measurement procedure

In batch conditions, respective volumes of aluminum stock solution, reagents and hydrochloric acid were mixed in a test tube. After the reaction time, which was specified during the optimization step, the absorbance was measured in a quartz 10 mm cuvette.

In the SIA system, respective volumes of aluminum standard solution, aluminon and other solutions were aspirated through the respective ports of the selection valve to the mixing coil by the loading movement of the syringe pump. Then the flow direction was reversed and thus the mixed zone with the complex of aluminum ions with aluminon was transferred to the flow cell and the absorbance signal was detected. All of the flow measurements were carried out in triplicate and the mean value was used for data evaluation.

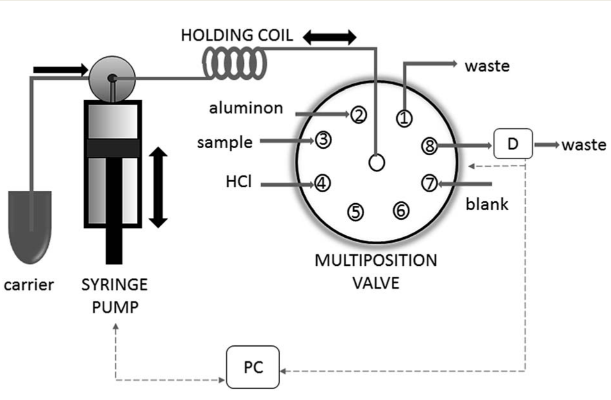

Fig. 1 Geometry of the SIA system.

Optimization – batch and flow conditions

At first, the absorbance spectra of aluminon and the complex of aluminon with aluminum ions were measured. The maximum wavelength absorbance shifted from 450 nm (aluminon) to 525 nm (complex with aluminum ions). Thus in all of the batch and flow experiments these two wavelengths were monitored. In the batch experiment reaction conditions including the pH adjustment, reaction time and the effect of ultrasound were tested.

The pH adjustment was tested by the addition of 1 M hydrochloric acid in the range of 0.5–3.0 mL (in 0.5 mL increments) using a ratio of 5 : 1 : 1 of aluminum stock solution : 1 M hydrochloric acid : aluminon solution. The final volume was kept at 10 mL by the addition of water. The absorbance was measured after 10 min and was corrected to the blank measurement when the aluminum solution was replaced with water. The same experiment was carried out using an ultrasound bath. The test tubes were placed in the bath for the 10 min reaction time.

Then the reaction time was tested in the range of 1–10 min (using 1 min increments) and 0.5 mL of 1 M hydrochloric acid was used throughout these experiments. The reaction time test was also carried out in the ultrasound bath to compare the obtained absorbance values.

In the SIA system (flow conditions) zones of 50 μL aluminum standard, 30 μL aluminon solution and 10 μL 1 M hydrochloric acid were aspirated. The first experiment was zone sequence testing. Six different zone sequences were tested with respect to the difference between the measured and blank signals.

Then the volume of 1 M hydrochloric acid was optimized in the range of 5–35 μL. The next optimization was devoted to the aluminon solution concentration – stock solution and it was diluted in the ratios of 1 : 2, 1 : 3, 1 : 4 and 1 : 5 with water.

In the flow system, the complex of aluminum ions with aluminon settled on the walls of the PTFE tubes. Thus a washing step was added to each measurement cycle using 0.1 M hydrochloric acid.

In the flow experiments, a non-symmetric peak shape was found. To solve this problem, additional mixing of the aspirated zones in the mixing coil was applied. Aspiration of the zones; sample, aluminon and hydrochloric acid were followed with the zone of 100 μL of water and then two flow reversals (two 50 μL increments) were applied to get efficient mixing.

Interference testing

Potential interfering ions (NH_4^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, NO_3^-, SO_4^{2-}, PO_4^{3-}, Cl^-, F^-, S^{2-}) were chosen with respect to the sample matrix (surface and drinking water) to include all commonly occurring ions and ions that should have interfered with the used complex reaction. Cations were tested in the form of chlorides or nitrates and anions were used as sodium salts and the respective tested concentration was added to the 200 μg L^{-1} aluminum standard solution. Evaluation of the ions' effect was carried out to find the level of interference that caused changes not exceeding 5% of the measured signal compared to the same concentration of aluminum ions in the standard solution (200 μg L^{-1} represents the limit of aluminum ions content in drinking water).

In the case of the low concentration level aluminum ion sample, pretreatment (addition of thioglycolic acid) was recommended and this will be discussed in detail.

Calibration

Linearity of calibration in the range of 10–1000 μg L^{-1} of aluminum ions was studied with respect to the linear range wide enough to accomplish real sample analysis. Limits of detection and quantitation were evaluated as a concentration, corresponding to 3-times and 10-times standard deviation of the blank signal.

Repeatability (intra and inter-day precision)

Repeatability was tested at two concentration levels (200 and 600 μg L^{-1} of aluminum ions) using RSD values for evaluation. 10 injections of standards were analyzed in parallel and the RSD value obtained was used for the repeatability (intra-day precision) evaluation. Inter-day precision was tested for 3 consecutive days and again 10 parallel injections of both standard solutions were analyzed.

The limit of repeatability was set to 5% which could be considered too high compared to sophisticated instrumental methods, but in case of quick and simple automated techniques developed for routine analysis, it was found to be sufficient.

Real samples

9 real samples from different sources (including well and pond waters) in the region of East and South Bohemia were tested. All samples were kept at 4 °C without any preservation and were analyzed 1 week after collection. The evaluation of real sample analyses was carried out by comparison with a 3-point calibration (100, 200 and 300 μg L^{-1} of aluminum standard solution).

With 2 real samples, the recovery test was accomplished to exclude potential matrix effects. The limit of recovery at the two concentration levels (100 and 200 μg L^{-1} of aluminum ions) was set to 100 ± 5%.

The content of aluminum ions found in all of the real samples was compared with the simple colour test (aluminium test, Aquaquant) which enabled a similar range of aluminum ion levels testing (70–800 μg L^{-1} of aluminum ions), using the colour reaction with chromazurol S. Evaluation of aluminum content was accomplished by a simple visual comparison of the colour intensity with comparative spots after a 7 min reaction period. Taking into account the different sensitivities of the developed automated method and the semiquantitative colour test (evaluation of the aluminum level based on the 8 concentration ranges in the mentioned scale), a comparison of the results obtained by these two methods was carried out.

Results and discussion

Preliminary investigations

Several preliminary experiments were carried out in batch conditions: the appropriate volumes of the aluminum working solution, aluminon and hydrochloric acid were mixed in the test tubes and the absorbance was measured in a 10 mm quartz cuvette. In batch conditions, the pH adjustment by the addition of hydrochloric acid showed only a slight increase in the absorbance for 0.5 mL of 1 M hydrochloric acid compared to reaction without any adjustment. When using higher volumes of 1 M hydrochloric acid (1.5–3.0 mL), the absorbance quickly decreased to 15%.

The reaction time was studied to get basic information about the reaction kinetics and its possible shortening in the flow system where a steady-state is not required. Coloured product formation was found to be so quick, that even after the first minute of the reaction the measured absorbance values were high enough (Fig. 2). In both cases (with and without ultrasound) absorbance values close to 0.9 were reached.

Investigation of the experimental conditions in the flow system

The evaluation of the data was based on the difference between the signal of the analyte and the blank. Testing the sequence of aspirated zones showed that the greatest difference in the obtained signals was in the case of the aspiration of sample followed by the acid and then by the aluminon; therefore the sample should be acidified first and then the reaction with aluminon is more efficient. The increase of the absorbance value was significant – approximately a 90% higher signal was obtained compared to the worst sequence where acid was aspirated first followed by the sample and then aluminon, as the aluminon cannot react in fully acidified conditions. Then the volume of the acid zone was tested but the obtained values varied only a little and thus a short zone of acid was found (5 μL) to be sufficient to keep the reaction conditions.

Then the aluminon volume was studied. The highest absorbance difference was found for the 15 μL aluminon zone. But the peak shape was negatively affected, thus aspiration of two zones of aluminon with the sample in between (sandwich technique) was applied for better results. For further experiments, a first aluminon zone of 10 μL and a second with 15 μL was used to get symmetric signals with the absorbance high enough.

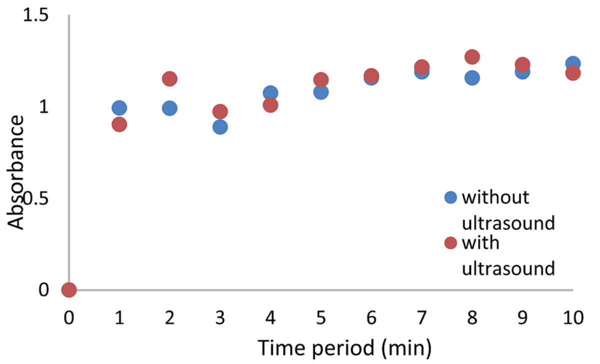

Fig. 2 Effect of the reaction time on the absorbance signal in batch conditions.

The final experimental conditions were found to be: sample pH, 4; zone sequence, 10 μL of aluminon–50 μL of sample–5 μL of 1 M HCl–15 μL of aluminon. The optimized flow rate values were: 50 μL s^{-1} for aspiration of the sample and reagents, 100 μL s^{-1} for efficient mixing (2 flow reversals using a 50 μL zone of distilled water) and 30 μL s^{-1} for the detection step.

Interference testing

An interference study was carried out and the results are summarized in Table 2, where non-interfering concentration mean concentration caused a change in absorbance lower than 5%. The developed determination is not affected by common ions present in real samples except for fluorides and ferric ions. However, the content of fluoride ions in the real water samples at an interfering level is not expected.

Concerning ferrous and ferric ions, their interference effect can be suppressed by the addition of thioglycolic acid, according to the recommendation suggested in the Technical norm 83 0520(22),[31] prior to sample aspiration into the flow system as the thioglycolic acid binds ferrous and ferric ions into stable non-interfering complexes. Thus the content of the free ionic form of these two ions was suppressed under the interfering level.

Calibration

Calibration range with LOD and LOQ limits were tested with standards containing 400 μL of 1% thioglycolic acid solution in 10 mL. Linearity of calibration was checked in the range of 100–800 μg L^{-1} of aluminum ions with a correlation coefficient of 0.9975.

The limit of detection and quantitation were 13.0 and 43.3 μg L^{-1}, respectively. The obtained calibration range, LOD and LOQ values were found to be sufficient for drinking water monitoring (the limit for aluminum ions in drinking water is 200 μg L^{-1}).

Repeatability, intra and inter-day precision

Repeatability at two concentration levels of aluminum ions (200 and 600 μg L^{-1}) was evaluated and the obtained results corresponded with a set limit of 5% RSD. The obtained RSD values for the lower and higher standard concentrations were in the range of 1.97–2.36% and 1.69–2.57%, respectively. The record of the repeatability measurement is demonstrated in Fig. 3.

The inter-day precision was evaluated as RSD values of the difference in the absorbance of the analyte and the blank during 3 days. At the 600 μg L^{-1} Al(III) level, the RSD was 2.93% which is excellent in the case of automated flow techniques. However, at 200 μg L^{-1} Al(III), the RSD exceeded the limit, and a 12.00% RSD value was obtained (in the case of low aluminum ion concentrations a comparison of the sample with a standard measured at the same time is recommended).

Analysis of real samples

Real samples of well and pond surface water were analyzed and the obtained results were compared with the simple colour test (aluminium test, Merck). The obtained results (Table 3)

Table 2 Results of interference study of common ions

Tested ion	Non-interfering concentration[a] [mol L^{-1}]	Non-interfering concentration[a] [mg L^{-1}]
Na^+	0.10	2298
NH_4^+	0.05	5349
Ca^{2+}	0.03	1002
Mg^{2+}	0.01	303
Pb^{2+}	0.025	5180
Fe^{2+}	**1.25×10^{-3}**	**69.8**
Fe^{3+}	**1.25×10^{-4}**	**6.98**
Cl^-	0.05	1772
F^-	**5×10^{-5}**	**0.949**
NO_3^-	0.01	775
SO_4^{2-}	0.05	4802
PO_4^{3-}	0.025	2425
S^{2-}	2.50×10^{-3}	160

[a] Concentration that caused change not exceeding 5% compared to 0.2 mg L^{-1} of aluminum ion standard absorbance.

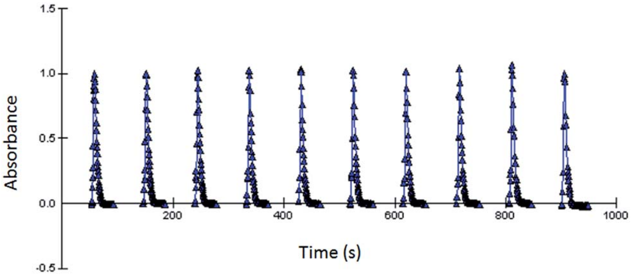

Fig. 3 Record of the repeatability measurement of aluminum ions at the 600 μg L^{-1} level.

corresponded well with the levels evaluated using the colour test in all cases of the samples.

Recovery values for the two concentration levels were checked to assure that the matrix effects were really eliminated by the addition of thioglycolic acid using two real samples (numbers 1 and 7, both were samples of well water from different localities). The results are summarized in Table 4 and showed sufficient recovery values for both samples. Thus the elimination of ferrous and ferric ions that were present in sample 7, where iron tubes were employed, was proved. When sample 7 was measured without any sample preparation, it provided an absorbance signal in reaction with aluminon that corresponded to a 20-times higher amount of aluminum ions than in the measurement after thioglycolic acid addition.

Table 3 Real samples analysis – evaluation of aluminum ion concentration[a]

Sample no.	Matrix	SIA mg L^{-1}	RSD [%]	Colour test mg L^{-1}
1	Well	0.0395	0.86	0–0.07
2	Pond	0.0480	0.80	0–0.07
3	Well	ND	—	ND
4	Well	0.0242	1.41	0–0.07
5	Well	ND	—	ND
6	Well	0.0327	1.34	0–0.07
7	Well	0.0124	0.21	ND
8	Well	ND	—	ND
9	Well	ND	—	ND

[a] ND – not detected (below LOD).

Comparison of sensitivity, selectivity and sample throughput

Matrix effects in the aluminum determinations of different types are always discussed because of the different selectivity of individual complex reagents.[16,19–21] In the present article aluminon was used as a reagent and the reaction was found to be sensitive enough for the analysis purpose even in non-steady state reaction conditions. Only in samples containing ferrous or ferric ions did the measured absorbance not correspond to the aluminum concentration. Elimination of this interference was very simple and was done by the addition of thioglycolic acid. In the case of fluorides which create complexes of different compositions with aluminum ions, interference was observed in all previous determinations too. It was found in some previous determinations that complex reactions could suffer from worse recoveries.[16,19,20] But in the case of the quick automated methods (where the reaction time is limited) used for screening reasons or monitoring of aluminum levels in similar sample matrices this drawback was not so crucial.

The linear range of the proposed spectrophotometric method did not cover as broad a range of concentrations than some other spectrofluorometric determinations (see Table 1)

Table 4 Recovery test[a]

		Standard		Sample		
Sample no.	C [mg L^{-1}]	A	RSD [%]	A	RSD [%]	R [%]
1	0.1000	0.088	2.02	0.091	0.76	103.41
	0.2000	0.231	3.19	0.231	4.48	100.00
7	0.1000	0.087	2.53	0.087	0.40	100.00
	0.2000	0.204	3.02	0.207	0.54	101.47

[a] A – difference of measured and blank signals; C – standard addition level; R – recovery.

Table 5 Comparison of the presented batch, flow and comparative (colour test) methods for aluminum ions determination

	Batch	Flow	Colour test
Linear range [μg L^{-1}]	20–1000	100–800	70–800
LOD	11.9	13.0	70
LOQ	29.0	43.3	70
Analysis time	10 min	1.5 min	7 min
Portability	No	Yes	Yes
Monitoring	No	Yes	No

but it still enabled the analysis of aluminum concentrations close to the limit for drinking water which was the main aim of the presented method. Samples with potential contamination of aluminum ions (localities close to industrial areas) could be always diluted for precise determination. And if such samples exceed the limit for aluminum ion content, then the suggested method proved to be sufficiently sensitive to select such samples. The obtained sample throughput was comparable to the other methods based on sequential injection or flow injection systems.[16,19–22] However the most rapid determination in time-based multisyringe FIA systems was more efficient and the analysis throughput was extremely high (154 h^{-1}).[17] In general aluminum determination in the SIA systems is more economical with respect to the decreased consumption of reagents and waste production compared to the FIA technique.

The recently published aluminum determination based on the SIA technique[29] showed a more complicated system where a reaction chamber with a 30 s stop-flow period to get the reaction product was used. Additionally a cleaning step of the reaction chamber prolonged the analysis to 220 s which meant a sample throughput of 16 h^{-1}. Thus the developed determination was found to be simpler and quicker for routine monitoring purposes.

A comparison of the described batch, flow and comparative methods with respect to linearity, LOD and LOQ limits and applicability to real on-site measurements was also carried out. The obtained values are summarized in Table 5 and showed a similar linear range to all of the mentioned methods, the LOD and LOQ limits of the flow method were higher than the respective values for the batch method which is commonly expected for non-steady state measurements, but there was higher sample throughput in the case of the flow method. The flow and comparative methods could be used for on-site measurements but in terms of long-term monitoring of the aluminum ion content in water sources only the flow method could be applied.

Conclusions

A simple and quick determination of aluminum ions in a sequential injection system for the analysis of water samples was described. Aluminon was used for the complex reaction and the spectrophotometric detection of coloured product was applied. Detailed optimization proved that the reaction speed enabled transfer to the automated flow system. An interference study showed the matrix effect in the case of fluorides (complexed with aluminum ions) and of ferrous and ferric ions (complexed with aluminon). The presence of ferrous and ferric ions in well water samples was expected (iron tubes), thus elimination was needed and accomplished by the addition of thioglycolic acid prior to analysis in the flow system. Determination of 9 real well and pond samples was compared with the colour test for aluminum ion determination based on a different colour reaction (chromazurol S). All of the results obtained in the flow system were found to be on the same level as the concentration ranges evaluated by the chromazurol test.

The developed automated method could be used for the simple and quick on-site measurement of aluminum content in water sources. Only a small amount of sample and reagent (50 μL, 25 μL) is consumed by one injection and the analysis time is 1.5 min which corresponds to a 13 samples per hour throughput in the case of triplicate sample aspiration.

The comparison of the linear range, LOD and LOQ showed lower sensitivity than AAS or methods with preconcentration by extraction techniques. But in the case of common water samples where the limit of the aluminum ion content is close to the limit for drinking water the described method has been proved to have sufficient sensitivity and selectivity for the routine analysis of large sample series or automated on-site monitoring of surface water samples.

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