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## ARTICLE

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

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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

## Introduction

Level of aluminum ions in different sample matrices was discussed frequently during the last period. The aim of the presented work is not based on toxicological effects of aluminum on human health but on simple and quick fully automated aluminum ions determination in water samples. Automation of inorganic species determinations in water quality control was 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 fully automated systems, quick analysis without need to reach reaction steady-state, with decreased consumption of reagents and acceptable repeatability. And additionally flow system could be used for different reasons not only detection but also sample pre-treatment including preconcentration, separation or extraction procedures.

The transfer of simple but validated manual determinations to the flow systems is relatively slow but some of them mainly based on continuous flow analysis (CFA) and FIA were accepted by national authorities and even included into the European technical norms. Determination of nitrites and nitrates was the first water quality control method that could be carried out in both mentioned flow

## Notes

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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 the 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 technique and lower consumption of reagents and samples in case of the SIA determinations and also lower waste production. On the other hand drawbacks could be found in lower sample throughput that is based on bi-directional movement of the piston pump in SIA compared to continuous flow in the FIA systems where more than one hundred of samples per hour could be injected.

Concerning aluminum ions determination many automated methods have been developed using different complex reactions and spectrophotometric or spectrofluorometric detections in the FIA or SIA systems. Spectrophotometric determinations were based mainly on pyrocatechol violet, eriochrome cyanine and aluminon. Sensitivity and selectivity of these colour reactions is well known and were discussed with respect to their application in the flow injection system and 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 reaction with 8-quinolinol-derivatized Fractogel where LOD at 70 nM and linear

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

Reagent	linear range	LOD	LOQ	sample throughput [h <sup>-1</sup> ]	citation
8-quinolinol	0.3 - 16 μM	70 nM			[14]
eriochrome cyanine	10.8 - 650 μg L <sup>-1</sup>	3.24 μg L <sup>-1</sup>		30	[15]
8-hydroxyquinoline -5-sulphonic acid	17.8 - 300 g L <sup>-1</sup>		18.1 g L <sup>-1</sup>	20*	[16]
8-hydroxyquinoline -5-sulphonic acid	10 - 500 g L <sup>-1</sup>	0.5 g L <sup>-1</sup>		154	[17]
morin	2 - 250 μg L <sup>-1</sup>	3.1 μg L <sup>-1</sup>		90	[18]
morin	50 - 1000 ppb	3 ppb		11*	[19]
8-hydroxy-7-(4-sulfo -1-naphthylazo)-5-quinoline sulphonic acid	100 - 800 ppb	4 ppb		20*	[20]
<i>N</i> - <i>o</i> -vanillidine	up to 1000 g L <sup>-1</sup>	0.057 g L <sup>-1</sup>		30	[21]
-2-amino- <i>p</i> -cresol					
quercetin	0.02 - 0.50 mg L <sup>-1</sup>	0.007 mg L <sup>-1</sup>	0.024 mg L <sup>-1</sup>	60	[22]
lumogallion	up to 1.1 μM	6.1 nM		17	[23]
morin	10 - 100 μg L <sup>-1</sup>	0.24 μg L <sup>-1</sup>			[24]
8-hydroxyquinoline	0.06 - 15 μg L <sup>-1</sup>	0.05 μg L <sup>-1</sup>		40	[28]
cinnamoyl derivative	55 - 660 μg L <sup>-1</sup>	4 μg L <sup>-1</sup>		16	[29]
<i>aluminon</i>	100 - 800 μg L <sup>-1</sup>	13.0 μg L <sup>-1</sup>	43.3 μg L <sup>-1</sup>	36	presented

\* measured in triplicate

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

Nowadays many fluorometric determinations could 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. Linear range of this determination was 17.8 - 300 μg L<sup>-1</sup>, limit of quantitation (LOQ) 18.1 μg L<sup>-1</sup>, repeatability 1.52%, recovery for real samples analysis was 92% and sample throughput 20 h<sup>-1</sup> [16]. The same complex reagent was used in time-based multisyringe FIA system where fluorescence detection was enhanced by micellar medium and thus linear range was broadened to 10 - 500 μg L<sup>-1</sup>, limit of detection (LOD) 0.5 μg L<sup>-1</sup>, and by parallel analysis of 3 injections sample throughput of 154 h<sup>-1</sup> was reached [17]. On-line monitoring of aluminum content in drinking water with fluorometric detection based on the reaction with morin with the LOD at 3.1 μg L<sup>-1</sup>, linearity in the range of 2 - 250 μg L<sup>-1</sup> and sample throughput of 90 h<sup>-1</sup> was also reported [18].

Micellar media enhancement of the fluorescence signal was applied for the SIA determination in drinking water based on aluminum-morin complex too. The mentioned reaction was linear in the range of 50 - 1000 μg L<sup>-1</sup>, LOD was 3 μg L<sup>-1</sup>, with acceptable recovery (91 - 97%) and sample throughput of 16 h<sup>-1</sup> [19]. Derivative of quinolone sulfonic acid was used also in another work where similar calibration range of 100 - 800 μg L<sup>-1</sup> and LOD of 4 μg L<sup>-1</sup> were obtained together with recovery of 92 - 101% and samples throughput of 16 h<sup>-1</sup> [20].

Different reagent - *N*-*o*-vanillidine-2-amino-*p*-cresol - was tested in the FIA system where similar linear range but lower LOD (0.057 μg L<sup>-1</sup>) were found [21]. Even different flow injection strategy based on reverse FIA where injection of sample was replaced by injection of reagent to the sample stream and tested with high sample throughput of 60 h<sup>-1</sup> but lower sensitivity - linear range was 20 - 500 μg L<sup>-1</sup>,

LOD and LOQ 7 and 24 μg L<sup>-1</sup>, respectively [22]. And novel approach for magnetic stirring-assisted dispersive liquid-liquid microextraction was tested for aluminum determination too [23].

Outside the field of automated analytical techniques spectrofluorometry was widely used for aluminum assays. To overcome problems with high sample matrix effects separation/pre-concentration method was recently described and used for aluminum determination in drinking water and biological samples (human hair) [24]. And green pre-concentration 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 floating organic drop was applied with enrichment factor of 128 [25]. 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 fluorides complexes was accomplished by ion chromatography [27]. Other determination was based on combination of liquid-based dispersive micro-extraction with stopped-flow spectrofluorometry applied for 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 cinnamoyl derivative was optimized in the sequential injection system and applied for determination in spiked water samples and pharmaceutical formulations [29].

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

The proposed automated SIA method was based on reaction with specific complex reagent *aluminon* that is characterized by quick

formation of red complex with aluminum ions in pH 4 (batch conditions). Following the technical norm (83 0520(22)) [31] absorbance is scanned after 15 min of heating and cooling down to room temperature. But in our preliminary batch experiments kinetics of this reaction was found to be fast enough for transfer to the flow system. Simple, and after ferrous and ferric ions matrix effects elimination, selective reaction to aluminum determination in surface water samples was described. Linear range, LOD, LOQ and sample throughput were mentioned together with the previously published flow determinations based mainly on spectrophotometric and spectrofluorometric detections (summarized in Table 1). The proposed method was applied for 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; ultra-pure water produced by a Millipore Milli-Q RG system (Millipore, USA) was used throughout the work. Aluminum chloride used as aluminum ions standard was purchased from Lachema (Czech Republic). Aurintricarboxylic acid ammonium salt (aluminon) applied 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%) used to suppress interfering effect of ferrous and ferric ions was obtained from Sigma-Aldrich (Czech Republic).

Aluminum ions stock solution was prepared dissolving aluminum chloride in water ( $100 \text{ mg L}^{-1}$  of aluminum ions); the working solutions were diluted to obtain concentrations in the range of  $20\text{--}1000 \text{ } \mu\text{g L}^{-1}$  of aluminum ions. Reagent working solution was prepared dissolving  $0.09 \text{ g}$  of aluminon in  $10.00 \text{ mL}$  of water, followed by mixing with solution of  $13.30 \text{ g}$  of ammonium acetate in  $10.00 \text{ mL}$  of water and with  $12.60 \text{ mL}$  of  $1 \text{ M HCl}$  and filled up to  $25 \text{ mL}$  in volumetric flask. Following preparation procedure found in technical standard (Technical norm 83 0520(22), [31]) only higher concentration of reagent ( $3.6 \text{ g L}^{-1}$  instead of  $0.9 \text{ g L}^{-1}$  of aluminon applied in batch conditions), that is commonly needed in 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. Solution of thioglycolic acid added to real samples were prepared by dilution with water to get 1% solution.

The colour test used for comparison of real samples determinations - Aluminium test, Aquaquant, was obtained from Merck (Germany).

### Apparatus

The setup corresponded to a commercially available FIALab<sup>®</sup> 3000 system (FIALab<sup>®</sup> Instrument Systems Inc., USA) with a syringe pump (syringe reservoir  $5 \text{ mL}$ ), a central eight-port Cheminert selection valve and a  $70 \text{ cm}$  long PTFE tubing reaction coil ( $0.50 \text{ mm i.d.}$ ). 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  $10 \text{ mm}$

path length was used for detection. The latest version of the FIALab<sup>®</sup> software (version 5.9.312) was employed for system control and data acquisition. The geometry of the SIA system is depicted in the Figure 1.

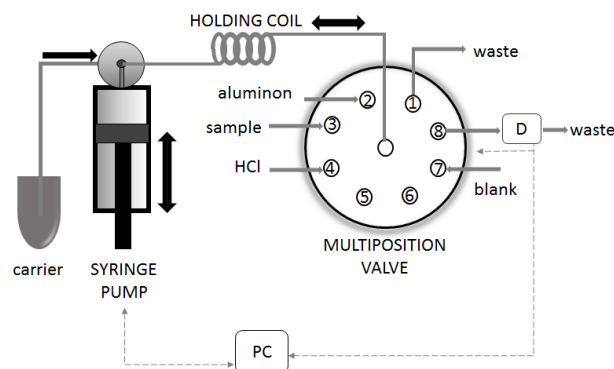


Figure 1: Geometry of the SIA system

Batch experiments were carried out in test tubes and absorbance was measured using 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 reaction time, which was specified during the optimization step, absorbance was measured in quartz  $10 \text{ mm}$  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 loading movement of the syringe pump. Then the flow direction was reversed and thus mixed zone with complex of aluminum ions with aluminon was transferred to the flow cell and absorbance signal was detected. All the flow measurements were carried out in triplicate and the main value was used for data evaluation.

### Optimization – batch and flow conditions

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

The pH adjustment was tested by addition of  $1 \text{ M}$  hydrochloric acid in the range of  $0.5\text{--}3.0 \text{ mL}$  (in  $0.5 \text{ mL}$  increments) using ration of  $5 : 1 : 1$  of aluminum stock solution :  $1 \text{ M}$  hydrochloric acid : aluminon solution. The final volume was kept by addition of water to  $10 \text{ mL}$ . Absorbance was measured after  $10 \text{ min}$  and was corrected to the blank measurement when aluminum solution was replaced with water. The same experiment was carried out using ultrasound bath. The test tubes were placed to the bath for  $10 \text{ min}$  of the 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 carried out also in ultrasound bath to compare the obtained absorbance values.

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

Then volume of 1 M hydrochloric acid was optimized in the range of 5 - 35  $\mu\text{L}$ . The next optimization was devoted to aluminon solution concentration – stock solution was diluted in the ratios of 1:2, 1:3, 1:4 and 1:5 with water.

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

In the flow experiments non-symmetric peak shape was found. To solve this problem additional mixing of aspirated zones in the mixing coil was applied. Aspirated zones of sample, aluminon and hydrochloric acid were followed with the zone of 100  $\mu\text{L}$  of water and two flow reversals (two 50  $\mu\text{L}$  increments) were applied to get efficient mixing.

### Interference testing

Potential interfering ions were chosen with respect to the sample matrix (surface and drinking water) to include all commonly occurring ions and ions those were supposed to interfere with the used complex reaction -  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{S}^{2-}$ . 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 200  $\mu\text{g L}^{-1}$  aluminum standard solution. Evaluation of ions effect was carried out to find the level of interference that caused changes of the measured signal not exceeding 5% compared to the same concentration of aluminum ions in standard solution (200  $\mu\text{g L}^{-1}$  represents the limit of aluminum ions content in drinking water).

In case of low concentration level of aluminum ions sample pre-treatment (addition of thioglycolic acid) was recommended and will be discussed in detail.

### Calibration

Linearity of calibration in the range of 10 – 1000  $\mu\text{g L}^{-1}$  of aluminum ions was studied with respect to the linear range wide enough to accomplish real samples analyses. Limits of detection and quantitation were evaluated as a concentration corresponded to 3-times and 10-times standard deviation of the blank signal.

### Repeatability (intra and inter-day precision)

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

Limit of repeatability was set to 5% that could be too high compared to sophisticated instrumental methods but in case of quick and simple automated technique developed for routine analysis was found to be sufficient.

### Real samples

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

With 2 real samples the recovery test was accomplished to exclude potential matrix effects. Limit of recovery in two concentration levels (100 and 200  $\mu\text{g L}^{-1}$  of aluminum ions) was set to 100  $\pm$  5%.

Content of aluminum ions found in all real samples was compared with simple colour test (Aluminium test, Aquaquant) that enabled similar range of aluminum ions levels testing (70 – 800  $\mu\text{g L}^{-1}$  of aluminum ions) using colour reaction with chromazurol S. Evaluation of aluminum content was accomplished by simple visual comparison of colour intensity with comparative spots after 7 min reaction period. Taking into account different sensitivity of the developed automated method and the semiquantitative colour test (evaluation of aluminum level based on 8 concentration ranges in the mentioned scale) 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 aluminum working solution, aluminon and hydrochloric acid were mixed in the test tubes and the absorbance was measured in 10 mm quartz 10 mm cuvette. In batch conditions pH adjustment by addition of hydrochloric acid showed only slight increase of the absorbance for 0.5 mL of 1 M hydrochloric acid compared to reaction without adjustment. Using higher volumes of 1 M hydrochloric acid (1.5 – 3.0 mL) absorbance quickly decreased to 15%.

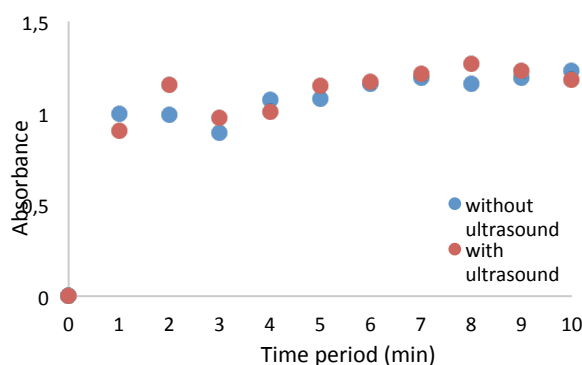


Figure 2: Effect of the reaction time on the absorbance signal in batch conditions

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

### Investigation of the experimental conditions in flow system

The evaluation of data was based on the difference of the signal of analyte and blank. Testing the sequence of aspirated zones proved the highest difference in the obtained signals in the case of aspiration of sample followed by acid and then aluminon; the sample should be acidified at first and then reaction with aluminon is more efficient. The increase of absorbance value was significant – about 90% higher signal was obtained compared to the worst sequence where acid was aspirated at first and then sample and aluminon cannot react in fully acidified conditions. Then the volume of acid zone was tested but the obtained values varied only a little and thus short zone of acid was found to be sufficient to keep reaction conditions (5  $\mu\text{L}$ ).

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

The final experimental conditions were found to be: sample pH, 4; zone sequences, 10  $\mu\text{L}$  of aluminon - 50  $\mu\text{L}$  of sample - 5  $\mu\text{L}$  of 1 M HCl - 15  $\mu\text{L}$  of aluminon. Optimized flow rates values were: 50  $\mu\text{L s}^{-1}$  for aspiration of sample and reagents, 100  $\mu\text{L s}^{-1}$  for efficient mixing (2 flow reversals using 50  $\mu\text{L}$  zone of distilled water) and 30  $\mu\text{L s}^{-1}$  for detection step.

Table 2: Results of interference study of common ions

Tested ion	Non-interfering concentration* [mol L <sup>-1</sup> ]	Non-interfering concentration* [mg L <sup>-1</sup> ]
Na <sup>+</sup>	0.10	2298
NH <sub>4</sub> <sup>+</sup>	0.05	5349
Ca <sup>2+</sup>	0.03	1002
Mg <sup>2+</sup>	0.01	303
Pb <sup>2+</sup>	0.025	5180
Fe <sup>2+</sup>	<b>1.25 x 10<sup>-3</sup></b>	<b>69.8</b>
Fe <sup>3+</sup>	<b>1.25 x 10<sup>-4</sup></b>	<b>6.98</b>
Cl <sup>-</sup>	0.05	1772
F <sup>-</sup>	<b>5 x 10<sup>-5</sup></b>	<b>0.949</b>
NO <sub>3</sub> <sup>-</sup>	0.01	775
SO <sub>4</sub> <sup>2-</sup>	0.05	4802
PO <sub>4</sub> <sup>3-</sup>	0.025	2425
S <sup>2-</sup>	2.50 x 10 <sup>-3</sup>	160

\* concentration that caused change not exceeding 5% compared to 0.2 mg L<sup>-1</sup> of aluminum ions standard absorbance

### Interference testing

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

fluoride ions in the real water samples in interfering level is not expected.

Concerning ferrous and ferric ions, their interference effect can be suppressed by 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 to bind ferrous and ferric ions to the stable non-interfering complexes. Thus content of 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  $\mu\text{L}$  of 1% thioglycolic acid solution in 10 mL. Linearity of calibration was checked in the range of 100 – 800  $\mu\text{g L}^{-1}$  of aluminum ions with correlation coefficient of 0.9975.

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

### Repeatability, intra and inter-day precision

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

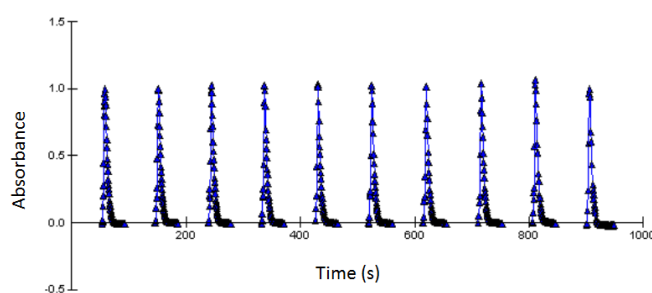


Figure 3: Record of the repeatability measurement of aluminum ions in 600  $\mu\text{g L}^{-1}$  level

Inter-day precision was evaluated as RSD values of the difference in the absorbance of analyte and blank during 3 days. At 600  $\mu\text{g L}^{-1}$  Al(III) level, the RSD was 2.93% that is excellent in case of automated flow techniques. However, at 200  $\mu\text{g L}^{-1}$  Al(III), the RSD exceeded the limit, and 12.00% RSD was obtained (in case of low aluminum ions concentrations comparison of sample with 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) corresponded well with levels evaluated using the colour test in case of all samples.

Table 3: Real samples analysis – evaluation of aluminum ions concentration

Sample No.	matrix	SIA		Colour test mg L <sup>-1</sup>
		mg L <sup>-1</sup>	RSD [%]	
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

ND – not detected (below LOD)

Recovery values in two concentration levels were checked to assure that matrix effects were really eliminated by addition of thioglycolic acid using two real samples (numbers 1 and 7, both samples of well water from different localities). Results were 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. Sample 7 measured without any sample preparation provided absorbance signal in reaction with aluminum corresponded to 20-times higher amount of aluminum ions than in measurement after thioglycolic acid addition.

Table 4: Recovery test

Sample No.	standard		sample		R [%]
	C [mg L <sup>-1</sup> ]	A RSD [%]	A RSD [%]	A RSD [%]	
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 – difference of measured and blank signals; C – standard addition level; R - recovery

### Comparison of sensitivity, selectivity and sample throughput

Matrix effects in aluminum determinations of different types are always discussed because of different selectivity of individual complex reagents [16, 19-21]. In the presented article aluminum 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. Just in samples containing ferrous or ferric ions measured absorbance did not correspond to aluminum concentration. Elimination of this interference was very simple using addition of thioglycolic acid. In case of fluorides that create complexes of different compositions with aluminum ions interference was observed in all previous determinations too. Complex reactions could suffer from worse recovery that was found in some of previous determinations [16, 19-20]. But in case of 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.

Linear range of the proposed spectrophotometric method covered not so broad range of concentrations than some of spectrofluorometric determinations (see Table 1) but still enabled to analyze aluminum concentrations close to the limit for drinking water that was the main aim of the presented method. Samples with potential contamination

with aluminum ions (localities close to industrial areas) could be always diluted for precise determination. And if such samples will exceed the limit for aluminum ions content suggested method was 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, 19-20, 21-22]. However the most rapid determination in time-based multisyringe FIA system was more efficient and analysis throughput was extremely high (154 h<sup>-1</sup>) [17]. In general aluminum determination in the SIA systems are 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 more complicated system where reaction chamber with 30 s stop-flow period to get the reaction product was used. Additionally a cleaning step of the reaction chamber prolong the analysis to 220 s that means the sample throughput of 16 h<sup>-1</sup>. Thus the developed determination was found to be more simple and quick for routine monitoring purposes.

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 were summarized in Table 5 and showed similar linear range of all the mentioned methods, LOD and LOQ limits of the flow methods higher than the respective values for batch method (that is commonly expected for non-steady state measurements) but higher sample throughput in 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 aluminum ions content in water sources only the flow method could be applied.

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 <sup>-1</sup> ]	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

### Conclusions

Simple and quick determination of aluminum ions in sequential injection system for analysis of water samples was described. Aluminum was used for complex reaction and spectrophotometric detection of coloured product was applied. Detailed optimization proved reaction speed that enables transfer to the automated flow system and setting all reaction conditions. Interference study showed matrix effect in case of fluorides (complex with aluminum ions), ferrous and ferric ions (complex with aluminum). Content of ferrous and ferric ions in well water samples was expected (iron tubes) thus elimination was needed and accomplished by addition of thioglycolic acid prior to analysis in the flow system. Determination of 9 real well and pond samples was compared with colour test for aluminum ions determination based on different colour reaction (chromazurol S). All results obtained in the flow system were

found on the same levels as concentration ranges evaluated by the chromazurol test.

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

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

### Acknowledgements

This publication was supported by the Charles University in Prague (Project SVV 260 184) and is co-financed by the European Social Fund and the state budget of the Czech Republic, project No. CZ.1.07/2.3.00/20.0235, the title of the project: TEAB. J.Š. is grateful to the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and Slovak Academy of Sciences for supporting by Grant no. 1/0226/11.

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