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A RAPID AND GREEN FLOW INJECTION METHOD FOR THE SPECTROPHOTOMETRIC DETERMINATION OF Al IN AQUEOUS MATRICES

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ABSTRACT

A novel spectrophotometric method for the determination of aluminium (III) in aqueous samples was developed, validated, and optimized, based on the complex formation, between the analyte and Chromo Azurol S using flow injection (FI) system. A five-factor central composite design (CCD) using the response surface methodology (RSM) was employed to optimize the experimental reaction variables. The resulting second order polynomial model was found to be highly statistically significant, confirming its excellent fit to the experimental data. Under the optimized conditions, the method shows satisfactory accuracy and precisión. The method s robustness was confirmed using a Youden-Steiner test, and was applied and validated to tap water samples. The FI method shows advantages over the batch conventional operation, such as high sensitivity, low volume simple consumption, and high sample throughput (40 samples hr $^{-1}$). Also achieved a high analytical greenness metric (AGREE) and blue applicability grade index (BAGI), which confirms its ecological quality and practicality. This work provides a rapid, cost-effective, and reliable analytical tool for the determination of aluminium in aqueous matrices.

Keywords: Aluminium, flow injection, response surface methodology.

1. INTRODUCTION

Aluminium (Al) is the third most abundant metal in the Earth's crust. Its wide distribution and unique properties have led to its extensive use across various industries, including food, pharmaceuticals, and construction, as well as in water treatment processes [1]. However, this widespread use also results in a high degree of human exposure, which has become a significant public health concern. As a non-biodegradable contaminant, Al has the potential for accumulation in human tissues, and an excessive intake has been associated with several serious pathological disorders. Early evidence of its toxicity emerged in the 1970s, when a link was established between high Al levels in dialysis water and its accumulation in the cerebral and bone tissues of patients [2]. Subsequent research has implicated chronic Al exposure in several human disorders, including neurological conditions such as Alzheimer's and Parkinson's diseases, as well as osteomalacia and certain types of anemia [3,4]. Human exposure to Al occurs through the natural content of food and water, which is often increased by acid rain or the use of commercial aluminium salts as flocculants in water treatment plants. Furthermore, Al is a key ingredient in personal care products, such as deodorants and antiperspirants [5]. The potential health risks[5], highlights the need for reliable analytical methods. While various techniques have been developed for Al determination in different matrices, including spectrophotometry [6-16], spectrofluorimetry and differential pulse adsorptive stripping voltammetry (DPAdSV)[17], atomic absorption spectrometry (GF) [18,19], chemiluminescence [20], and ICP-MS [21], many of these methods suffer from limitations typical of batch analysis, such as low sample throughput and high reagent consumption.

This study addresses the need for a reliable analytical method by proposing the use of a Flow injection (FI) system with spectrophotometry for the determination of Al^{3+}. The method is based on the complexation reaction between Al^{3+} and the chromogenic reagent Chrome Azurol S (CAS) [22]. The system's performance will be optimized by investigating key parameters related to both instrumental detection sensitivity and complex formation conditions [23]. By improving the Al^{3+}-CAS complex formation and detection conditions, this work aims to develop a more sensitive and efficient method for Al determination in tap water samples.

2. EXPERIMENTAL

2.1. Reagents.

A stock solution of CAS (1.00 x 10^{-3} mol L^{-1}) was prepared by first dissolving 60.53 mg in deionized water and then diluting to the mark of 100 ml in a volumetric flask. Working standards were freshly prepared by diluting the stock solution in deionized water to obtain the required concentrations. Aqueous solutions of aluminium (Al^{3+}) 1.00 x 10^{-3} mol L^{-1}, acetic acid (CH_3CO_2H) 1.00 mol L^{-1}, buffer acetic acid/ sodium acetate 0.60 mol L^{-1} and sodium hydroxide (NaOH) 1.00 mol L^{-1} were prepared from PA Merck reagents.

2.2. Instruments.

Spectral measurements were recorded in the range between 190 and 800 nm against a blank using a Perkin Elmer Lambda 35 double beam spectrophotometer with matched quartz cells (10 mm). The spectral data were processed using the Perkin Elmer UV WinLab data processor and viewer software (version 1.00). An analytical balance (AS 60/220/C/2, ± 0.01 mg) and a pH-meter (Hanna) were also used.

The determination was conducted using a two-channel FI manifold comprised of a peristaltic pump (Ismatec 834C), an injection valve (VICI Cheminert C22-3186EH), 0.8 mm i.d. silicone rubber tubing, connecting joints, and a flow cell (Figure 1). The sample containing the analyte was injected on a carrier stream (composed of buffer and CAS solution), then dispersed into the reaction coil, and directed towards the detector flow cell. This configuration enabled well defined FI signals, which facilitated studies for the optimization of the method.

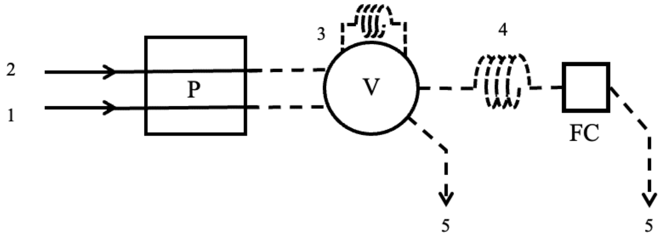

Figure 1. Experimental flow injection manifold with molecular absorption spectrometric detection. Carrier **(1)**, sample **(2)**, sample injection volume (V_i) **(3)**, reaction volume (V_r) **(4)**, waste outlet **(5)**, peristaltic pump **(P)**, injection valve **(V)**, and quartz flow cell with 1 cm optical path **(FC)**.

2.3. Procedures

2.3.1. Batch

A stock solution of CAS (1.00 x 10^{-3} mol L^{-1}) was prepared by dissolving 60.53 mg in deionized water and diluting to 100 mL in a volumetric flask. Working standards were freshly prepared by diluting the stock solution in deionized water to achieve the required concentrations. Aqueous solutions of Al^{3+} 1.00 x 10^{-3} mol L^{-1}, CH_3CO_2H 0.60 mol L^{-1}, buffer acetic acid/ sodium acetate 0.60 mol L^{-1} and NaOH 1.00 mol L^{-1} were prepared from PA Merck reagents.

To evaluate the influence of pH and buffer concentration, analogous experimental conditions were utilised, incorporating varying buffer concentrations (1.80 x 10^{-2}, 3.60 x 10^{-2}, and 9.00 x 10^{-2} mol L^{-1} at pH 4.60) and pH values (4.53, 4.60, 4.75, and 5.01 with 1.80 x 10^{-2} mol L^{-1} buffer).

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Under experimental conditions, the kinetic stability of the Al^{3+}-CAS complex was examined using, concentrations of Al^{3+} 4.00 x 10^{-6} mol L^{-1}, CAS 2.50 x 10^{-5} mol L^{-1}, and buffer 1.80 x 10^{-2} mol L^{-1} at two pH values of 4.60 and 5.01. For 30 minutes, absorbance at 546 nm was measured at 1minute intervals.

2.3.2. FI-spectrophotometric method

Al^{3+} was determined using the following experimental variables: a buffer concentration from 8.90 10^{-3} to 1.80 10^{-2} mol L^{-1}, a CAS concentration from 1.28 x 10^{-5} to 2.50 x 10^{-5} mol L^{-1}, a V_i between 100 and 200 µL, and a V_r between 327 and 654 µL. The Al^{3+} concentration was held constant at 8.00 x 10^{-6} mol L^{-1}. Three F were tested: 0.810, 1.62, and 2.03 mL min^{-1}. All FI assays were performed under optimized conditions, with the response signal monitored at 546 nm relative to the reagent blank (carrier). The experiment used 1 cm pathlength quartz flow cell (volume 50 µL) and comprised five injections for each sample. All experiments were conducted at ambient temperature.

2.3.3. Optimization by response surface methodology

For the optimization of the proposed methodology, response surface methodology (RSM) with a central composite design (CCD) was employed to evaluate the response surface. To maximize the analytical signal and achieve a wider linear range, five independent variables were investigated over the following ranges: CAS (5.00 10^{-6}–2.50 10^{-5} $molL^{-1}$), and buffer (3.00 x 10^{-4} –1.75 x 10^{-2} mol L^{-1}), V_i (100 – 300 µL), V_r (150 – 300 µL), and F (1.01 – 1.82 mL min^{-1}). Each variable was studied at five coded levels, designated as -2, -1, 0, +1, and +2. All experimental runs were performed according to the CCD matrix, with the concentration of Al^{3+} held constant at 8.00 x 10^{-6} mol L^{-1}. The experimental data from the CCD were subjected to multiple linear regression (MLR) analysis. To model the measured response, a second-order quadratic polynomial equation was proposed, which includes linear, quadratic, and interaction terms. This equation is represented as:

$$A = \beta_0 + \sum_{i=1}^{k} (\beta_i x_i + \beta_{ii} x_i^2) + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j \quad (Eq.\ 1)$$

In this model, *A* represents the absorbance response, and k is the number of independent variables (k = 5). The terms x_1, x_2, x_3, x_4, and x_5 are the coded values for the independent variables: CAS concentration, buffer concentration, V_i, V_r, and F, respectively. The corresponding regression coefficients for the constant, linear, quadratic, and interaction terms are denoted by β_0, β_i, β_{ii}, and β_{ij}. The statistical significance and predictive capability of the fitted model were rigorously evaluated using analysis of variance (ANOVA). The experimental data from the CCD-RSM were analyzed using design of experiments software (Modde 7). The resulting response surface plots were used to identify the optimal conditions for achieving the maximum analytical signal.

2.3.4. Calibration curve in standard solutions and proposed samples.

The calibration curves for both standard solutions and tap water samples were prepared at Al^{3+} concentrations ranging of 6.00 x 10^{-6} to 2.00 x 10^{-5} mol L^{-1}. The standard curve was prepared using deionized water, whereas the tap water curve was developed with pre-treated tap water. Each sample solution was injected into a carrier stream maintained at pH 5.00, with CAS and buffer concentrations consistently held at 2.00 x 10^{-5} and 4.60 x 10^{-3} mol L^{-1}, respectively. All calibration measurements were performed under the optimal system settings, with absorbance values measured relative to a reagent blank that was adjusted to a zero-absorbance. A linear curve was obtained, and the analytical parameters were evaluated based on 30 replicates of the lowest concentration. Accuracy and precision parameters were assessed through intra and inter-day tests conducted over a five days' period for the following Al^{3+} concentrations: 6.00 x 10^{-6}, 8.00 x 10^{-6} and 1.20 x 10^{-5} mol L^{-1}.

Tap water samples were collected from the laboratory faucets and bottled in 500 mL polyethylene containers without any preservatives. To minimize contamination from the pipes, the water was allowed to drain for 15 minutes prior to collection. Analysis of the samples was performed within 5 hours of collection. To eliminate potential interference from suspended matter and dissolved gases, the samples were pre-treated by filtering through a 0.22 µm membrane and boiling for 15 minutes. Aliquots of these treated samples were then spiked with known concentrations of Al^{3+} for method validation.

2.3.5. Robustness

The method's ability to remain consistent despite finite changes was evaluated using the Youden-Steiner test. This evaluation provides an indication of the procedure's reliability under normal use.

2.3.6. Assessment of method greenness and practicability

The greenness and practicability of the FI method was assessed using the analytical greenness metric (AGREE) and the blue applicability grade index (BAGI) tools. AGREE is a comprehensive method that provides a pictogram with 12 sections, each corresponding to a principle of Green analytical chemistry. BAGI is a complementary metric that evaluates the method's overall practicality on a score of 25 to 100, with a higher score indicating greater practicality. Together AGREE and BAGI offer comprehensive assessment of the method's environmental impact and its real-world applicability.

3. RESULTS AND DISCUSSIONS

3.1. Influence of concentration and pH buffer

The increase of buffer concentration reduces the absorbance of the Al^{3+}-CAS complex at 546 nm. To illustrate this effect three buffer concentrations (1.80 x 10^{-2}, 3.60 x 10^{-2}, and 9.00 x 10^{-2} mol L^{-1}) were studied. This effect significantly impacts its spectral behaviour [24]. The spectrograms (Figure 2a) confirm that the absorption maximum remains fixed at 546 nm, with the highest absorbance observed at the lowest buffer concentration. Consequently, the buffer concentration of 1.80 x 10^{-2} mol L^{-1} was selected for further studies.

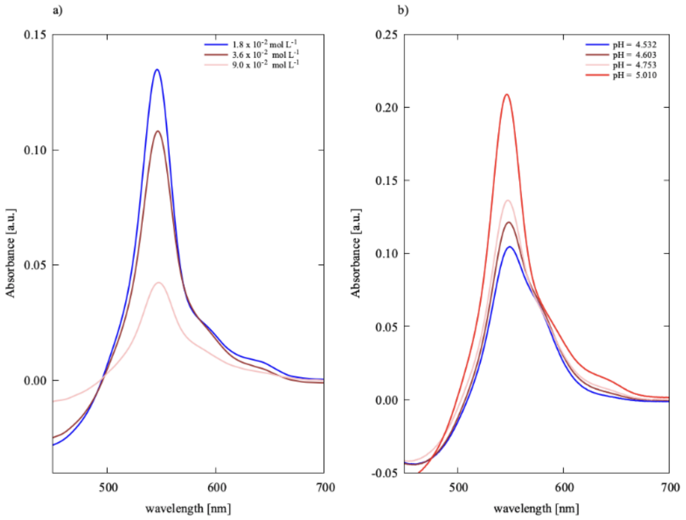


Figure 2. Absorption spectra with the effect of: **(a)** Buffer concentration (1.80 x 10^{-2}, 3.60 x 10^{-2}, and 9.00 x 10^{-2} mol L^{-1}) at pH 4,6, CAS 2.50 x 10^{-5} mol L^{-1} and Al^{3+} 4 x 10^{-6} mol L^{-1}. **(b)** pH (4.53, 4.60, 4.75 and 5.01) at buffer 1.8 x 10^{-2} mol L^{-1}, CAS 2.50 x 10^{-5} mol L^{-1} and Al^{3+} 4 x 10^{-6} mol L^{-1}.

The signal intensity of the Al^{3+}-CAS complex at 546 nm increases with pH, reaching a maximum at pH 5.8 before declining sharply. To investigate this effect, a pH range of 4.53 to 5.01 was tested. The results (Figure 2b) show that the maximum absorbance occurs at pH 5.01, with lower pH values yielding reduced signals. For enhanced sensitivity and continuity in this study, pH 5.01 was chosen as the optimal value.

3.2. Univariate assessment of experimental variables

The experimental results indicated that a F of 1.62 mL min^{-1} was the most appropriate. At lower F (e.g., 0.810 mL min^{-1}), the FI signals were broader, indicating greater dispersion and longer analysis times, which led to decreased peak height and sensitivity. While higher flow rates (2.03 mL min^{-1}) resulted in narrower and taller signals, this condition also helped extend the useful life of the FI manifold [25]. As a compromise between sensitivity and equipment preservation, a flow rate of 1.62 mL min^{-1} was selected for subsequent tests.

The results (Figure 3) showed that a buffer (pH 5.01) concentration of 8.90 x 10^{-3} mol L^{-1} yielded higher signals compared to 1.80 x 10^{-2} mol L^{-1}.

Larger reaction volumes produced broader signals due to longer residence times, whereas smaller reaction volumes resulted in narrower peaks [26]. Due to better mixing, an V_i of 200 µL produced higher absorbance. An V_r of 327 µL resulted in more defined signals and higher absorbance than 654 µL, likely due to improved homogeneity.

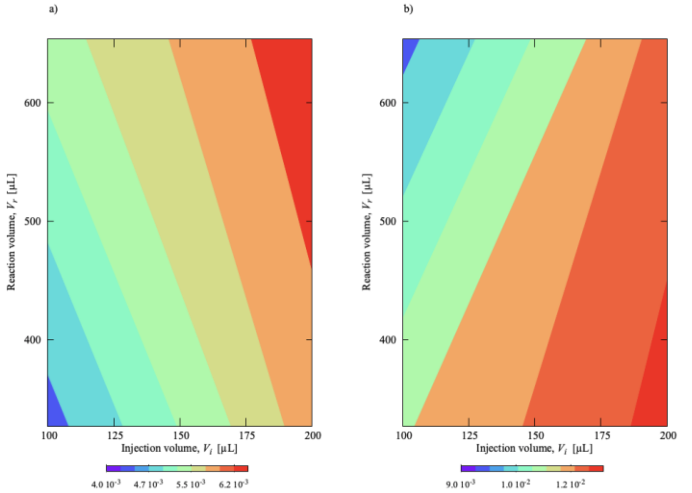


Figure 3. Influence on the FI signal of V_r with respect to V_i at F 1.62 mL min^{-1} and buffer pH= 5.01 **(a)** CAS, buffer, and Al^{3+} concentrations of 2.5 x 10^{-5}, 1.8 x 10^{-2}, and 8.00 x 10^{-6} mol L^{-1}, respectively. **(b)** CAS, buffer, and Al^{3+} concentrations of 1.28 x 10^{-5}, 8.9 x 10^{-3}, and 8.00 x 10^{-6} mol L^{-1}, respectively.

3.3. Optimization by response surface methodology

The quadratic model presented in Equation 1 was fitted to the central composite design (CCD) experimental data, and the resulting regression coefficients are summarized in Table 1. The linear coefficients for the CAS and Buffer concentrations are highly significant ($p < 0.001$). The positive coefficient for CAS concentration indicates that increasing its concentration enhances the analytical signal, as expected. Conversely, the negative coefficient for the buffer concentration suggests a detrimental effect on absorbance, possibly due to a quenching effect. Notably, while the linear terms for the hydraulic variables (V_i , V_r , and F) were not statistically significant ($p > 0.05$), their quadratic terms were highly significant ($p < 0.01$). The consistently negative sign of all quadratic coefficients for these variables, as well as for the CAS and buffer concentrations, confirms the presence of a concave response surface with a maximum within the experimental domain. The resulting reduced quadratic model provided an excellent fit for the experimental data and was found to be highly statistically significant ($p < 0.001$), confirming a strong relationship between the independent variables and the absorbance response. This is further supported by a high coefficient of determination, indicating that 99.4% of the variability in the absorbance can be explained by the model. The adjusted R^2 value is also very high, suggesting that the model is robust and not overfitted. The model's predictive capability is further substantiated by a cross-validated Q^2 value of 0.655, which is well above the acceptable threshold and demonstrates the model's reliability in predicting new data points. The lack-of-fit test, which compares the model's error to the pure error from the replicated experiments, was found to be non-significant ($p = 0.616$). This indicates that the reduced quadratic model adequately describes the relationship between the variables and the response, and there is no evidence to suggest that a higher-order model is needed. The low residual sum of squares (1.62 x 10^{-11}) further confirms that the experimental data points are very close to the values predicted by the model. In summary, these statistical metrics confirm that the developed model is both a statistically significant and highly accurate representation of the experimental system.

Table 1: Regression coefficients and analysis of variance of the quadratic and reduced quadratic model.

Model Term	Coeff		Std. Err.	p-value	CI
Intercept	β_0	-1.99	1.01 x 10^{-6}	6.36 x 10^{-31}	2.61 x 10^{-6}
x_1	β_1	6.99 x 10^{-6}	5.26 x 10^{-7}	4.30 x 10^{-5}	1.35 x 10^{-6}
x_2	β_2	-1.14 x 10^{-5}	7.80 x 10^{-7}	2.74 x 10^{-5}	2.00 x 10^{-6}
x_3	β_3	7.35 x 10^{-7}	4.86 x 10^{-7}	0.191	1.25 x 10^{-6}
x_4	β_4	-5.16 x 10^{-7}	4.86 x 10^{-7}	0.337	1.25 x 10^{-6}
x_5	β_5	-2.57 x 10^{-7}	7.89 x 10^{-7}	0.758	2.03 x 10^{-6}
x_1^2	β_{11}	-2.66 x 10^{-6}	3.85 x 10^{-7}	9.74 x 10^{-4}	9.89 x 10^{-7}
x_2^2	β_{22}	-2.44 x 10^{-6}	5.51 x 10^{-7}	6.83 x 10^{-3}	1.42 x 10^{-6}
x_3^2	β_{33}	-2.42 x 10^{-6}	3.85 x 10^{-7}	1.49 x 10^{-3}	9.89 x 10^{-7}
x_4^2	β_{44}	-1.56 x 10^{-6}	3.85 x 10^{-7}	9.89 x 10^{-3}	9.89 x 10^{-7}
x_5^2	β_{55}	-3.92 x 10^{-6}	5.49 x 10^{-7}	8.32 x 10^{-4}	1.41 x 10^{-6}

After optimization, the final configuration of the FI method was established with the following values: CAS concentration of 2.00 x 10^{-5} mol L^{-1}, buffer concentration of 8.90 x 10^{-3} mol L^{-1}, V_i of 150 µL, V_r of 200 µL, and F of 1.30 mL min^{-1}. These values represent the optimal factor levels determined by the model's output to maximize the analytical response.

The stoichiometric relationship of the Al^{3+}–CAS complex was determined using the slope ratio method. The resulting slope ratio was 25.80: 22.68, which corresponds approximately to a molar ratio of 1.14:1 (Al^{3+}: CAS). This value indicates that the stoichiometry of the complex formation is very close to 1:1.

3.4. Calibration and analytical performance

Optimal conditions for obtaining the maximum analytical signal were determined from CCD study, and the resulting linear and analytical parameters are presented in Table 2. The significance of the linear correlation was assessed using a two-tailed Student's t-test. The calculated t-statistic was found to be greater than the critical value ($t_{calculated} > t_{critical}$) at a 95% confidence level, which led to the rejection of the null hypothesis (H_0) and confirmed a statistically significant linear relationship between the absorbance and Al^{3+} concentration.

Recovery rates for both intraday and interday measurements are detailed in Table 3. The recoveries, which ranged from 99.4% to 100.3%, demonstrate satisfactory accuracy for the developed analytical method. Precision was also confirmed with a Student's t-test at a 95% confidence level. For all evaluated concentrations, the calculated t-statistic was less than the critical value ($t_{calculated} < t_{critical}$), indicating that the differences between the observed and expected values are within acceptable limits. This confirmed the satisfactory repeatability and precision of the method.

Table 2: Analytical parameters.

Parameters	Standard solutions	Tap water
A	-2.11×10^{-2}	-2.16×10^{-2}
B	5.12×10^{2}	5.18×10^{2}
R^2	0.999	0.999
LOD (mol L^{-1})	4.56×10^{-7}	4.44×10^{-7}
LOQ (mol L^{-1})	1.38×10^{-6}	1.34×10^{-6}
Linear Range (mol L^{-1})	$4.56 \times 10^{-7} - 2.00 \times 10^{-5}$	$4.44 \times 10^{-7} - 2.00 \times 10^{-5}$
Std. Dev. (σ)	7.08×10^{-4}	6.96×10^{-4}
t_{calc}	200	70.7

LOD = 3.3 σ/m; **LOQ** = 10 σ/m; t_{cal} = Calculated t-value ($t_{critical}$ = 2.78); σ of 30 measurements of 6.00×10^{-6} mol L^{-1}.

Table 3. Intra-day and inter-day repeatability and reproducibility of the method for Al^{3+} determination.

Samples		Added 10^{-6} mol L^{-1}	Found 10^{-6}mol L^{-1}	RSD %	SE 10^{-8}	CL 10^{-8}	t_{cal}	Recovery (%)
Standard solutions	**Intra-day**	6.00	6.04	1.23	4.29	9.05	0.895	100.6
		8.00	7.95	1.07	4.92	10.4	0.998	99.4
		12.0	12.0	1.38	9.59	20.2	0.285	100.2
	Inter-day	6.00	5.98	1.28	4.42	9.32	0.384	99.7
		8.00	7.99	0.882	4.07	8.58	0.246	99.9
		12.0	12.0	1.29	8.95	18.9	0.378	100.3
Tap water	**Intra-day**	6.00	6.04	1.48	5.14	10.9	0.778	100.7
		8.00	8.00	0.279	1.29	2.72	0.0440	100.0
		12.0	12.0	2.12	14.7	31.1	0.0161	100.0
	Inter-day	6.00	6.02	0.504	1.75	3.70	1.07	100.3
		8.00	7.97	0.726	3.34	7.06	0.753	99.7
		12.0	12.0	1.30	9.01	19.0	0.188	100.1

RSD: Relative standard deviation; **SE:** Standard error; t_{cal}: Calculated t-value ($t_{critical}$=4.30); **CL:** Confidence limit at 95% .

3.5. Validation and application

The developed method was validated using spiked tap water samples. Potential interferences from both organic and inorganic matter, as well as dissolved gases, were effectively eliminated through the sample preparation procedure detailed in the Experimental section. The analytical parameters derived from this calibration are summarized in Table 2.

To evaluate accuracy and precision, recovery rate assays were conducted on the spiked samples. The recovery rates for both intra-day and inter-day measurements, performed over 5 consecutive days with 30 blanks, were found to be in the ranges of 100.0–100.7% and 99.7–100.3%, respectively, demonstrating satisfactory accuracy (Table 3). Statistical analysis using a Student's t-test at a 95% confidence level confirmed that there was no significant difference between the true and measured concentrations, further validating the accuracy of the method in tap water.

The calibration curves for standard solutions (deionized water) and spiked samples (tap water) showed excellent linearity with negligible scattering and no significant proportional or translational effects. According to the criteria established by Ellison and Thompson [27], these results indicate that the sample treatment procedure was highly effective at removing matrix interferences, thus ensuring the method's reliability.

3.6. Robustness

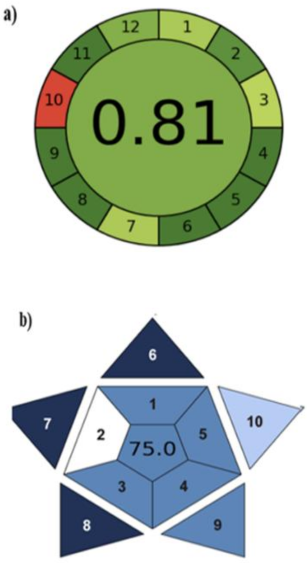
The method's robustness was evaluated using a Youden-Steiner test (Table 4). The results demonstrated that the difference between the studied values was less than the established comparison value, which confirms that the method is stable and reliable under the conditions analyzed. Consequently, the procedure is considered robust and suitable for normal use in tap water.

Table 4: Experimental results of Younden-Steiner robustness test.

Variable condition	High value (Z)	Low value (z)	$\bar{x}$ Z 10^{-2}	$\bar{x}$ z 10^{-2}	D (Z – z) 10^{-4}	D < $\sqrt{(2SD^*)}$ 10^{-4}
Analyst	2	1	1.96	1.91	5.00	4.52
Equipment	2	1	1.95	1.93	2.00	4.52
Equipment stabilization	1	0	1.95	1.93	2.00	4.52
Carrier stability	2	0	1.94	1.93	1.00	4.52
Buffer conc. (mol L^{-1})	4.64×10^{-3}	4.56×10^{-3}	1.96	1.93	3.00	4.52
CAS conc. (mol L^{-1})	2.03×10^{-5}	1.97×10^{-5}	1.95	1.94	1.00	4.52
Wavelength (nm)	545	547	1.95	1.93	2.00	4.52

3.7. Greenness and practicability profile

The greenness of the analytical procedure was evaluated using advanced tools, as recommended in the literature. The analytical greenness metric (AGREE) assessment, whose variables are flexible and can be weighted from 0 to 1 [28], reveals that the proposed method scores 0.81. The lowest score was assigned to the variable related to the source of reagents, which indicates an area with potential for a higher environmental impact (Figure 4 a). Furthermore, the blue applicability grade index (BAGI) was utilized to assess the practicality of analytical method [29]. It is recommended that the final score be higher than 60 to ensure the practicality of the procedure. In this case, the developed method received an overall score of 75.0 (Figure 4 b), confirming its high degree of applicability and practicality.



1. Sample treatment
2. Sample amount
3. Device positioning
4. Sample prep. stages
5. Automation, miniaturization
6. Derivatization
7. Waste
8. Analysis throughput
9. Energy consumption
10. Source of reagents
11. Toxicity
12. Operator

1. Type of analysis
2. Multi or single element analysis
3. Analitical technique
4.Simultaneous simple preparation
5. Sample preparation
6. Sample per h
7. Reagents and materials
8. Preconcentration
9. Degree of automation
10. Amount of sample

Figure 4. Evaluation of the proposed spectrophotometric FI method, using AGREE **(a)** and BAGI **(b)**, tools for greenness and blueness.

The developed method does not present the environmental drawbacks of other previously reported methods, which employ toxic reagents (eg, surfactant) and require complicated sample pretreatment. The respective AGREE values were 0.81 and 0.52, clearly demonstrating the greater greenness of the method developed in this research [16].

CONCLUSIONS

This study successfully developed and validated a new method for the spectrophotometric determination of aluminium in a flow injection system. By employing a central composite design (CCD) within a response surface methodology (RSM) framework, the complex interactions between the five key experimental variables were thoroughly optimized to achieve a maximum analytical signal. The resulting reduced quadratic model was found to be statistically significant, with a high coefficient of determination ($R^2 = 0.994$) and a non-significant lack-of-fit, confirming its robustness and accuracy in describing the experimental system.

The method's performance was validated through a rigorous analysis of its analytical parameters, including excellent accuracy (with recoveries between 99.4% and 100.3%) and satisfactory precision. The robustness of the method was confirmed using tap water samples, demonstrating its reliability for practical applications. Other advantages of the FI method are its high sensitivity, simple sample processing, low volume sample consumption, and high sample throughput (40 samples hr $^{-1}$).

The overall results from AGREE and BAGI assessments were satisfactory, confirming the method's excellent ecological profile and high degree of practicality. This work provides a straightforward, rapid, and cost-effective analytical tool for aluminium quantification but also serves as a strong case study for the effective use of chemometric optimization in the development of modern analytical methods.

CONFLICTS OF INTEREST

The authors state that there are no conflicts of interest related to the publication of this paper.

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