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Spectrophotometric determination of sulphate in automotive fuel ethanol by sequential injection analysis using dimethylsulphonazo(III) reaction

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Abstract

A sensitive SIA method was developed for sulphate determination in automotive fuel ethanol. This method was based on the reaction of sulphate with barium–dimethylsulphonazo(III) leading to a decrease on the magnitude of analytical signal monitored at 665 nm. Alcohol fuel samples were previously burned up to avoid matrix effects for sulphate determinations. Binary sampling and stop-flow strategies were used to increase the sensitivity of the method. The optimization of analytical parameter was performed by response surface method using Box–Behnker and central composite designs. The proposed sequential flow procedure permits to determine up to 10.0 mg SO_4^{2-} l^{-1} with R.S.D. <2.5% and limit of detection of 0.27 mg l^{-1}. The method has been successfully applied for sulphate determination in automotive fuel alcohol and the results agreed with the reference volumetric method. In the optimized condition the SIA system carried out 27 samples per hour.

Keywords: Sulphate determination; Automotive fuel ethanol; SIA; Ethanol combustion

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1. Introduction

A pioneer Brazilian alcohol program from sugar cane was implemented as a response to a 1970s oil crisis with intention of increase alcohol production for automotive biofuel purposes [1–4]. In the same decade a blend of 10% dry ethanol and unleaded gasoline (E10) was commercially introduced into the US and continues to be marketed mainly in the Midwestern states. Nevertheless, Asia is the largest potential producer of bioethanol [5], which is an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression–ignition engines [6].

In Brazil, the quality control of automotive fuel ethanol is accomplished by National Petroleum Agency, which specify of physical–chemical parameters such as electric conductivity, pH, density, chloride and sulphate contents. For ethanol production by fermentation of sugar cane biomass the pH is adjusted to 4–5 range with sulfuric acid addition to suppress growing of strange microorganisms [7]. On the other hand a suitable control at pH adjust and distillation stage is essential since low concentration level of sulphate in fuel ethanol can deactivate exhaust catalyst. The determination of sulphate in automotive fuel ethanol must be carried out by sufficiently sensitive method due to low level limit specified by Brazilian rules (4 mg kg^{-1}) [8].

Although the turbidimetric method related to barium sulphate production [9,10] is the more usual sulphate determination method, it does not present suitable low detection limits for this kind of application. In addition, some troubles to adapt this method to flow systems were related due to the low stability of $BaSO_4$ suspension and the risk associated to the retention of precipitate in flow transmission lines

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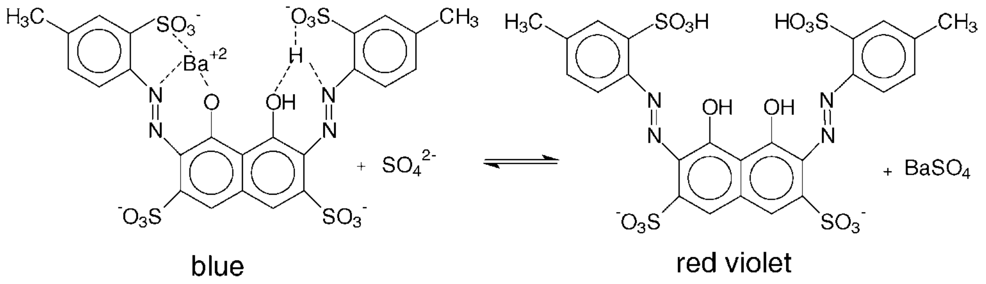

Scheme 1.

[11–14], leading to an increase of flow system complexity due to the addition of a new channel to insert suspension stabilizer reagents (e.g. polyvinyl alcohol) as well as the addition of a cleaning step to redissolve $BaSO_4$ deposits from flow lines with EDTA [11]. In particular, turbidimetric SIA systems based on $BaSO_4$ formation shown unsuitable limits of detection (10 mg l^{-1}) [13–15] for sulphate determination in fuel ethanol, since expected concentration for this analyte is below 4 mg l^{-1} [8].

Some available methods for sulphate determination with high sensitivity were related as colorimetric reaction with benzidine [16,17], methylthymol blue-zirconium [18], barium chloranilate [18–20], as well as the ion chromatography [9,21–23]. Most of these methods suffer from ethanol interference, high cost equipments or present difficult to be adapted to a flow system.

Sulphate ions reacts with barium–dimethylsulphonazo (III) complex, Ba-DMSA(III), displacing DMSA(III) and producing the low soluble barium sulphate (Scheme 1). The color solution changes from blue [Ba-DMSA(III)] to violet [DMSA(III)] and the sulphate content can be related to the increase of analytical signal at 550 nm or the decrease at 665 nm [24,25].

In this work a sequential injection analysis system is described for spectrophotometric determination of sulphate in automotive fuel ethanol using Ba-DMSA(III) and the signal measurements were monitored at 665 nm, due to the high sensitivity in this wavelength in comparison to 550 nm [24,25]. A pre-treatment for ethanol removal of alcohol samples were carried out by combustion. Optimization was accomplished by multivariate response surface method using Box–Behnker and central composite design [26].

2. Experimental

2.1. Reagents and solutions

All solutions were prepared from analytical grade reagents using deionised water with resitivity greater than 18 MΩ cm^{-1}.

Sulphate stock solution 1000 mg l^{-1} was prepared dissolving previously dried K_2SO_4 (Quimex, Brazil) in water. A solution of 8.7×10^{-5} mol l^{-1} DMSA(III) was prepared by dissolving the Na-DMSA(III) (J.T. Baker, Phillipsburg) in an solution of 7.6×10^{-5} mol l^{-1} Ba^{2+}, 5.0×10^{-4} mol l^{-1} KNO_3 (Quimex, Brazil), 1% (v/v) in acetic acid (Merck, Germany), 2.0 mg l^{-1} K_2SO_4 in 75% (v/v) ethanol (J.T. Baker, Mexico). The chromogenic reagent was stored in amber flask. Saturated nitron (Riedel-de-Haën) solution was prepared dissolving the reagent in 5% (v/v) acetic acid solution. Solution of Na_2CO_3 5% (m/v) and HCl 0.3 mol l^{-1} were prepared as usual.

Concomitants ions solution of carbonate 300 mg l^{-1} (Na_2CO_3), phosphate 1 mg l^{-1} (KH_2PO_4), chloride 5.0 mg l^{-1} (KCl), iron 10 mg l^{-1} ($FeCl_3$), sodium 5.0 mg l^{-1} ($NaNO_3$) and copper 0.4 mg l^{-1} (Cu^0, 0.1 M HNO_3) were prepared to evaluation of selectivity. The influence of potential interferences was studied employing references solutions with 0.0, 3.0 and 7.0 mg l^{-1} sulphate concentration.

2.2. Sample pre-treatment

In a 100 ml beaker 50 ml of fuel ethanol sample and 0.5 ml of 5% (m/v) Na_2CO_3 were added. The combustion ignition was carried out using a small piece of filter paper (Whatman 5) as a wick that was burned and cautiously thrown on fuel ethanol sample. When ethanol sample was burned until dryness (~20 min) 40 ml of water was added, shaken for 5 min to extract inorganic ions, transferred to a 50 ml volumetric flask and diluted to the mark with deionized water.

2.3. Apparatus

A multiposition valve Cheminert^{TM} 25C-3188EMH (Valco Instruments, Houston, USA) was employed to select and direct solutions. A spectrophotometer Femto 432 (S. Paulo, Brazil) equipped with borosilicate flow cell with 10 mm optical path and 200 μl cell volume. A peristaltic pump Gilson Minipuls 3 (Villiers-le-Bell, France) was employed for fluid propulsion. Isoversinic and PTFE tubes (0.8 mm i.d.) were used in flow system as peristaltic and transmission tubes, respectively. A gas diffusion device equipped with PTFE membrane was employed to prevent air bubbles in the flow cell, since bubbles are produced by changes on interfaces surface tension related to aqueous carrier and ethanolic reagent solution. A microcomputer Pentium I equipped with PCL 711S (Advantech, Taipei, Taiwan) was employed to con-

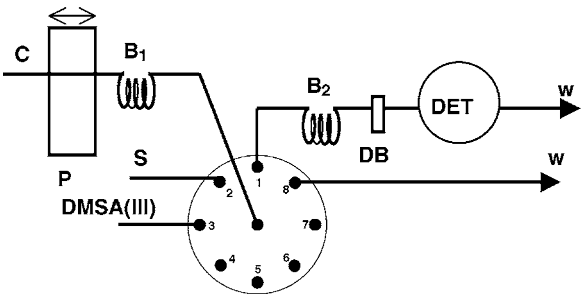

Fig. 1. Diagram of sequential injection manifold. C, carrier (H_2O); P, peristaltic pump; S, sample; DMSA(III), chromogenic reagent; DB, bubble remover; DET, spectrophotometer ($\lambda = 665$ nm); W, waste, B_1 and B_2 = sampling (500 cm) and reaction (200 cm) coils, respectively.

trol multiposition valve and peristaltic pump, as well as for signal acquisition.

2.4. Flow system

A schematic diagram of the flow manifold is shown in Fig. 1. Table 1 illustrates the steps for sulphate determination in fuel ethanol samples. Aliquots of pre-treated sample of fuel ethanol (S1) and DMSA(III) (S2) solutions were alternately aspirated to the sampling coil (B_1) following the binary sampling strategy [27] with the same volumetric proportion of the sample and reagent aliquots, where 45 aliquots of 3.3 μl of sample and chromogenic reagent solutions were loaded in tandem to improve mixing conditions. Thus, 150 μl was the total sample volume used per determination. The sample zone was directed to a reaction coil (B_2), by reverting the direction of peristaltic pump rotation (S3), and then the flow was stopped for 58.5 s to increase the reaction interval time without increasing dispersion (S4). Finally, the flow was reestablished and the mixture was sent to the flow cell (S5). The analytical signal was measured at 665 nm.

2.5. Standard method for sulphate determination

In order to compare the results obtained by the proposed method a reference volumetric method for sulphate determination in ethanol was employed [28]. In this method 100 ml of fuel ethanol sample, 50 ml of sulphate free absolute ethanol and 1 ml of 5% (m/v) Na_2CO_3 was added to a 500 ml rotavapor flask. This solution was evaporated until almost dryness at rotavapor bath at 65 °C and 70 mmHg. The residue was dissolved with 3 ml of 0.3 mol l^{-1} HCl and 3 ml of acetone. Finally, six drops of 2×10^{-3} mol l^{-1} DMSA(III) and two drops of saturated nitron solution were added and this solution was titrated with 0.01 mol l^{-1} $BaCl_2$ standard solution until end point color change from violet to blue.

Table 1
Steps for sulphate determination on SIA system

Step	Action	Valve position	Flow rate (ml min^{-1})[a]	Time (s)
S1	Sample loading	2	−1.0	0.2
S2	DMSA(III) insertion	3	−1.0	0.2
		–[b]	–	–
S3	Sending to reaction	1	+1.7	27
S4	Stop-flow	1	0.0	58.5
S5	Directing to detector	1	+1.7	60

[a] (+) pumping and (−) aspiration.

[b] The steps S1 and S2 were repeated for more 44 times.

3. Results and discussion

3.1. DMSA(III) concentration effect

The influence of DMSA(III) concentration on the analytical signal was evaluated maintaining the ration between the concentrations of DMSA(III) and Ba^{2+} in 1:0.7. The increase in DMSA(III) concentration from 5.0×10^{-5} to 8.7×10^{-5} mol l^{-1} provided an increase on net analytical signal. For DMSA(III) concentration higher than 8.7×10^{-5} mol l^{-1} it was not observed significant increase. On further experiments the reagents concentrations were maintained at 8.7×10^{-5} and 6.0×10^{-5} mol l^{-1} for DMSA(III) and $BaCl_2$, respectively.

3.2. pH effect of Ba-DMSA(III) reagent solution

The influence of pH in Ba-DMSA(III) reagent solution on net analytical signal was evaluated and higher sensitivity was obtained for the pH range from 3.5 to 5.5. In spite of the signal decrease for pH 3.5 of reagent solution (11%), it was selected in order to minimize interference from carbonate and phosphate ions [24,25].

3.3. Effect of the sulphate concentration in Ba-DMSA(III) solution

Barium sulphate precipitation can be induced by sulphate ions addition in Ba-DMSA(III) solution in order to oversupply the reagent solution with $BaSO_4$ [25], leading to supersaturation condition that favor removal of barium ions for the Ba-DMSA complex by sulphate. This procedure increase method sensitivity, reaction rate and reduce lower limit of linear range of concentration. On the other hand, for the proposed system conditions turbidity occurrence due to $BaSO_4$ formation are not expected [24,25] since in this reaction medium sulphate concentration is below 10 mg l^{-1} and in the presence of hydroalcoholic DMSA solution the precipitation of barium sulphate crystals were not detected by spectrophotometer at 665 nm. This can be explained by the slow growing of barium sulphate crystals in aqueous-ethanol medium.

The effects of sulphate concentration on analytical response can be observed in Fig. 2A and B. Fig. 2A exhibits the influence of sulphate concentration in reagent solution on the net analytical signal. The effect of sulphate concentration in Ba-DMSA(III) reagent solution on analytical curves

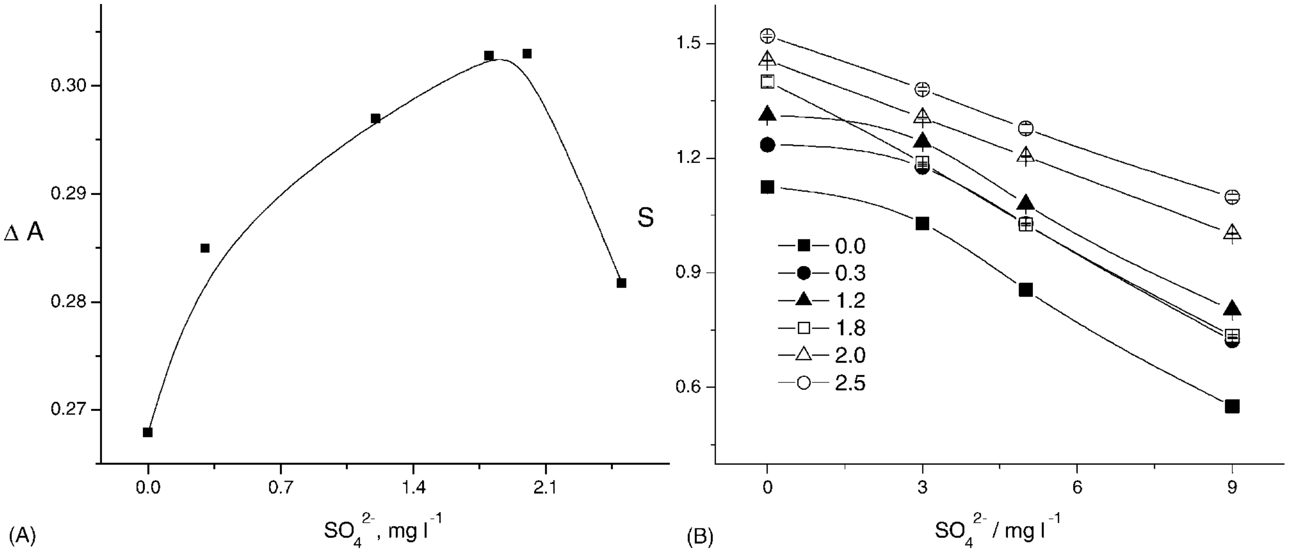

Fig. 2. Influence of $SO_4{}^{2-}$ concentration in chromogenic reagent on (A) net analytical signal and (B) linear range of analytical curves. The sulphate concentration is 6.0 mg l^{-1}.

can be seen in Fig. 2B. In order to improve analytical curves examination 0.15 absorbance units for different sulphate concentration was incremented to plot curves in Fig. 2B. For sulphate in reagent concentrations higher than 1.8 mg l^{-1} were not observed problems related to non-linearity for lower analyte concentrations in reference sulphate solution. In this way the sulphate concentration in Ba-DMSA(III) reagent was maintained at 1.8 mg l^{-1} to provide maximum sensitivity and minimize non-linearity problems.

3.4. Optimization by surface response method

Multivariate optimization was carried out using only flow variables due to difficulties associated to simultaneous evaluation of sensitivity and non-linearity problems, since the first is related to the procedure parameters while the second can be linked with chemical parameters of the reaction. The influence of flow rate ($flow_R$), reaction coil length ($loop_R$), sample volume (vol) and stop-flow time interval (t_{SF}) on sensitivity (ΔA) was evaluated by response surface method. A Box–Behnker design was employed for multivariate optimization and the levels of the evaluated variables are presented in Table 2. The response surface obtained by Box–Behnker design was described by the equation $\Delta A = 0.24 + 0.062t_{sf} - 0.018t_{sf}{}^2 + 0.071loop_R - 0.030loop_R{}^2 + 0.074vol - 0.023\,vol^2 + 0.009flow_R - 0.039\,flow_R{}^2 - 0.042t_{sf}loop_R - 0.008\,volflow_R$, with the variables at coded levels. The results obtained by Box–Behnker showed that the optimal point was not located at experimental dominium and the sensitivity could be increased by increasing the samples volume and reaction coil length.

Table 2
Experimental levels employed for optimization design

Variable	Coded variable		
	(−1)	(0)	(+1)
Sample volume (μl)	66.7	108.0	150.0
Reaction coil (cm)	20	120	220
Flow rate (ml min^{-1})	1.00	1.75	2.50
Stop-flow time (s)	0	60	120

However, for sample volumes higher that 150 μl it was frequently observed leakages at bubble remover device due to longer contact between aqueous alcoholic reagent and hydrophobic PTFE membrane. Then sample volume and reaction coil length were maintained at maximum values experimentally evaluated, 150 μl and 200 cm, respectively, to avoid leakages and to maintain the relationship between these variables that lead to sensitivity increase, since the linear coefficients of this variables are of the same magnitude.

Since the sample volume and reaction coil length were fixed at better practical conditions, only two parameters should be evaluated—flow rate and stop-flow time interval. As the Box–Behnker design must be applied for more than three variables, for the further experimental design it was constructed a central composite design to optimize the SIA procedure by response surface method. The response surface obtained by central composite design can be observed in Fig. 3 and it could be described by equation $\Delta A = 0.355 - 0.016t_{sf}^2 - 0.036flow_R{}^2$. The optimized values of flow variables obtained using central composite design are presented in Table 3.

3.5. Interference evaluation

Studies of interference for sulphate determination by SIA optimized procedure were performed for $CO_3{}^{2-}$, $PO_4{}^{3-}$, Cl^-, Fe^{3+} and Cu^{2+} and the results are presented in Table 4. For selected experimental conditions non-significant inter-

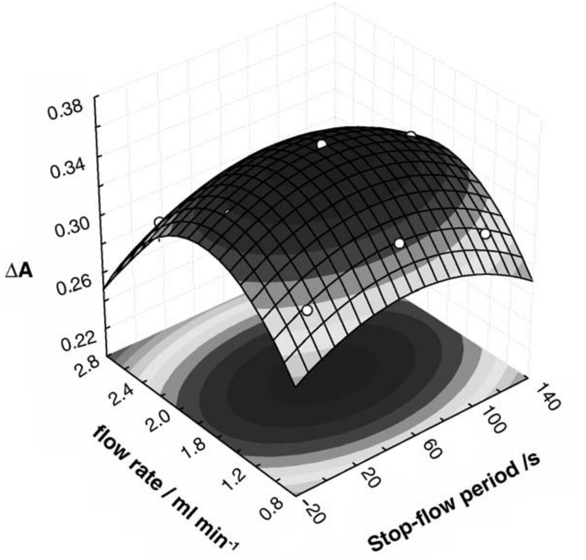

Fig. 3. Response surfaces obtained by central composite design for optimization of flow parameter.

Table 3
Optimized variables values by response surface method

Optimized parameters	
Sample volume (μl)	150
Reaction coil length (cm)	200
Flow rate (ml min^{-1})	1.7
Stop-flow period (s)	58.5

ference levels were obtained. It must be highlighted that the concentrations of evaluated potential interferences were much higher than those expected at fuel ethanol samples.

3.6. *Sample pre-treatment*

A persistent turbidity was observed when final composition of fuel ethanol sample after reagent addition contained more than 35% (v/v) of water. This turbidity level affects significantly the results for spectrophotometric determination of sulphate. Since preliminary experiments showed that DMSA(III) method requires at least 50% (v/v) of water to obtain significant signal variation for sulphate contents at expected concentration level in alcoholic fuel samples (<4 mg l^{-1}), a pre-treatment strategy must employed to remove the insoluble organic additives in aqueous media found in this kind of samples.

Initial experiments with filtration after reagent addition using 0.45 μm pore size filter paper of cellulose nitrate (Sartorius, Germany) for turbidity removal were tried and a poor repeatability and recovery on spike addition tests were obtained. Other strategies such as solvent evaporation on water batch or vacuum evaporation using rotavapor device suffer from deficiencies related to high time consume and limited number of simultaneous sample processing. Therefore, a combustion procedure was developed for ethanol elimination of fuel alcohol samples followed by water dissolution of residual obtaining a clear solution. This strategy was selected due to the low volatility of sulphate ion at gradual combustion conditions employed in these experiments. Nevertheless, the number of bioethanol samples that can be simultaneously prepared for sulphate determination by the batch procedure cannot be established. By applying the proposed pre-treatment 20 samples were almost simultaneously processed within 20 min without additional equipments, such as the rotavapor employed for the reference method [28].

3.6.1. *Sample volume of fuel ethanol sample employed for combustion*

The aliquot volume of fuel alcohol sample submitted to the combustion was evaluated. Sulphate lost and contamination during sample handling, analytical throughput and gases emissions during combustion are important parameters related to the settled sample aliquot volume. The results obtained at recovery tests for evaluation of sample volume effect at combustion are presented in Table 5 and quantitative

Table 4
Sulphate concentrations at interference presence ($n = 3$)

Interference	Sulphate (mg l^{-1})	
	Added	Found
CO_3^{2-}	0.00	0.10 ± 0.08
	3.00	3.07 ± 0.05
Fe^{3+}	0.00	−0.1 ± 0.1
	3.00	3.04 ± 0.08
Na^+	0.00	0.00 ± 0.06
	3.00	2.9 ± 0.1
Cl^-	0.00	0.21 ± 0.09
	3.00	2.89 ± 0.08
Cu^{2+}	0.00	−0.05 ± 0.06
	3.00	2.79 ± 0.03
$H_2PO_4^-$	0.00	0.0 ± 0.1
	3.00	3.13 ± 0.05

Table 5
Effect of sample volume of fuel ethanol submitted to combustion ($n = 3$)

Sample volume (ml)	Sulphate (mg l^{-1})		
	Added	Found	Recovery (%)
10	0.00	1.8 ± 0.3	–
	1.00	2.5 ± 0.4	70
20	0.00	1.9 ± 0.2	–
	1.00	2.8 ± 0.3	90
25	0.00	1.9 ± 0.2	–
	1.00	2.8 ± 0.2	90
30	0.00	1.94 ± 0.07	–
	1.00	2.92 ± 0.04	98
50	0.00	1.93 ± 0.06	–
	1.00	2.94 ± 0.05	101

recovery (>95%) were obtained for sample volumes higher than 30 ml with good repeatability (<4%). The occurrence of lower recovery and repeatability for sample volumes lower than 30 ml was related to the abrupt temperature increasing during the combustion and the analyte lost.

3.6.2. *Effect of Na_2CO_3 in samples for combustion*

The addition of carbonate to fuel alcohol samples before combustion has reduced analyte lost by volatilization and increased method precision [10,29]. The influence of carbonate concentration for sulphate recovery after combustion was evaluated by the addition of 0.5 ml of 100 mg l^{-1} sulphate solution to 50 ml of fuel sample and then to combustion. The recovery test results for different carbonate concentration levels are shown in Table 6. It was observed that increasing carbonate concentration before combustion the recovery percentiles was increased, since the tendency of volatile sulfur oxides production at higher temperatures was diminished by carbonate addition. For carbonate concentration higher that 4.7 mmol l^{-1} lead to quantitative sulphate recovery (>95%). Any baseline drift was observed after 8 h of operation, reinforcing the hypothesis that barium sulphate deposition in the flow cell walls did not occur.

Table 6
Effect of carbonate concentration in fuel ethanol at recovery of sulphate after combustion procedure ($n = 3$)

Sample	Carbonate (mmol l^{-1})	Sulphate (mg l^{-1})		
		Added	Found	Recovery (%)
1	0.0	0.00	0.4 ± 0.3	–
		1.00	0.8 ± 0.4	40
	0.9	0.00	0.7 ± 0.2	–
		1.00	1.4 ± 0.1	70
	2.4	0.00	1.1 ± 0.1	–
		1.00	2.0 ± 0.2	90
	4.7	0.00	1.15 ± 0.06	–
		1.00	2.18 ± 0.04	103
	6.6	0.00	1.26 ± 0.07	–
		1.00	2.22 ± 0.08	96
2	0.0	0.00	1.4 ± 0.3	–
		1.00	2.1 ± 0.4	70
	0.9	0.00	1.8 ± 0.1	–
		1.00	2.6 ± 0.1	80
	2.4	0.00	1.92 ± 0.08	–
		1.00	2.9 ± 0.1	98
	4.7	0.00	1.97 ± 0.03	–
		1.00	2.96 ± 0.02	99
	6.6	0.00	1.95 ± 0.05	–
		1.00	2.93 ± 0.04	98

3.7. *Evaluation of turbidity occurrence*

The evaluation of turbidity occurrence in reaction media was carried out with the spectrophotometric measurements in the isosbestic wavelength at 586 nm (Fig. 4A) where reference solutions and fuel samples previously burned were submitted to sulphate determination by SIA manifold. As reagent concentration is fixed, at isosbestic wavelength, any changes in analytical signal could be attributed to media turbidity. Turbidity evaluation are illustrated in Fig. 4B and it was concluded that analytical signals were comparable at 95% confidence level for all evaluated samples and references solutions, confirming that turbidity occurrence was minimized with proposed pre-treatment.

3.8. *Figures of merit*

The proposed procedure presented good precision with relative standard deviation lower than 3% for all deter-

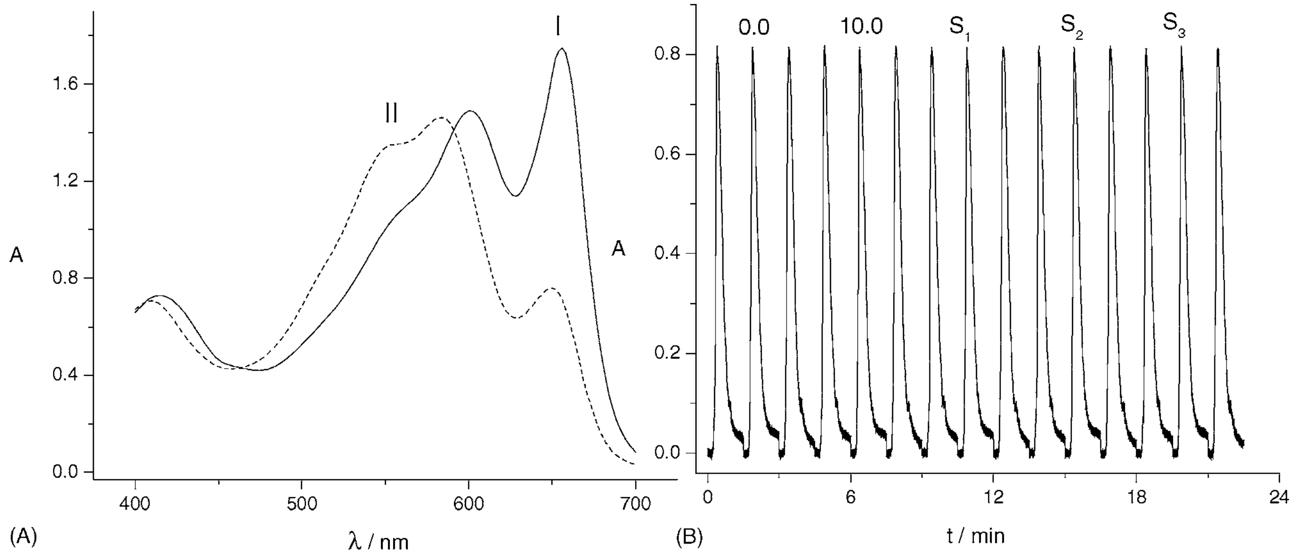

Fig. 4. Absorption spectra of Ba-DMSA(III) solution (A-I) and after 20 mg l^{-1} sulphate addition (A-II) for isosbestic wavelength location. Evaluation of turbidity occurrence at isosbestic wavelength (586 nm) for reference and sample solutions (B).

Table 7
Results obtained by SIA procedure and reference method for sulphate determination in fuel ethanol samples ($n = 3$)

Sample	Sulphate (mg kg^{-1})	
	SIA	Titration
A	3.77 ± 0.07	3.85 ± 0.05
B	3.6 ± 0.1	3.50 ± 0.07
C	4.29 ± 0.09	4.4 ± 0.1
D	1.68 ± 0.01	1.57 ± 0.09
E	2.14 ± 0.04	2.21 ± 0.05
F	1.37 ± 0.09	1.2 ± 0.1

minations and analytical throughput of 27 samples per hour. The limit of detection for sulphate was estimated at 0.27 mg l^{-1} ($n = 10$) by applying recommended criteria [30]. The linear range for sulphate determination was obtained up to 10.0 mg l^{-1} ($A = -0.051C + 0.962$, $R = 0.9995$).

3.9. Method validation

The proposed method was applied for sulphate determination in fuel ethanol samples. The results obtained by proposed method were compared with reference method and they agreed at 95% confidence level as shown in Table 7. Only one of the evaluated samples presented sulphate content higher than the limit imposed by Brazilian legislation (4 mg kg^{-1}) [8].

The titration reference method applied to validate the proposed SIA method showed some difficulties related to high sample volume consumption and laborious sample pretreatment. Additionally, the end point is hardly visualized that can be considered as a drawback to accept titration for routine bioethanol analysis.

4. Conclusions

The proposed method has shown powerful alternative for routine sulphate determination in automotive fuel ethanol samples. Combustion pre-treatment solved problems associated to turbidity occurrence permitting sample preparation within 20 min.

The proposed SIA system has shown high sampling rate, versatility, easy of process implementation, minimal sample handling, low reagent and sample consume and residue production. The consume of DMSA(III) was 1.3×10^{-5} mol per sample.

The proposed SIA method leads to lower sample handling and higher sampling throughput than the volumetric reference method. Additionally, the end point of biofuel ethanol titration is difficult to be visualized. By comparing the performance of proposed procedure and other flow systems designed for sulphate determination was observed that the proposed flow procedure presented higher selectivity and sensitivity and lower limit of detection. Therefore, the proposed procedure provides suitable conditions to determine sulphate in fuel ethanol samples.

Response surface method permitted the optimization of SIA parameters with a multivariate strategy using a reduced number of experiments. The presented automatic method for sulphate determination has shown good precision and accuracy.

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