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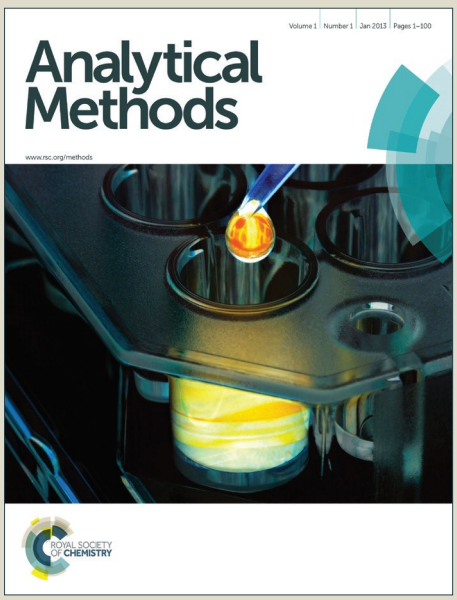

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Development of a Multicommuted Flow Analysis Procedures for Simultaneous Determination of Sulfate and Chloride in Petroleum Coke Employing a Homemade Syringe Pump and a LED-Based Photometer

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Abstract

The current paper deals with procedures for simultaneous determination of sulfate and chloride in petroleum coke samples after microwave-induced combustion (MIC), which were implemented employing a multicommuted flow analysis process. The setup comprised a homemade syringe pump and two individual flow system manifolds, each coupled to a homemade LED-based photometer. Dedicated software enabled sampling and reading steps to be performed while displacing the syringe pistons forward and backward, allowing a sampling rate of 150 determinations per hour. The procedure for sulfate determination was based on the reaction formation of barium with sulfate and turbidimetric detection, while the procedure for chloride determination was based on the photometric mercury/thiocyanate method. In order to investigate the feasibility of both the equipment setup and the proposed procedures, samples of petroleum coke previously digested by microwave induced combustion (MIC) were analyzed. For accuracy assessment, samples were also analyzed employing ion chromatography and inductively coupled plasma optical emission spectrometry to determine chloride and sulfate, respectively. The paired *t*-test indicated no significant difference between the results for our method and the established methods, at a 95% confidence level. Linear responses (r = 0.999) were obtained with concentrations ranging from 10 to 700 mg L^{-1} for sulfate, and from 0.25 to 10 mg L^{-1} chloride.

Keywords

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Syringe pump, Multicommuted flow analysis, Petroleum coke, Chloride and sulfate, Light emitting diode photometer, Green chemistry, Microwave induced combustion.

1. **Introduction**

Petroleum coke, a byproduct of the thermal processing of crude oil, has a high carbon content, including condensed aromatic rings, making it a useful feedstock for the gasification process.[1-5] Petroleum coke has also been used as a carbon source for the aluminum, refractory, and metallurgical industries.[6-8] Sulfate and chloride are among the main inorganic contaminants present in crude oils[9-11] and consequently in heavy products such as petroleum coke.

During the industrial processing of petroleum coke, sulfur compounds are released into the atmosphere, resulting in environmental damage, including the corrosion of metallic surfaces.[12,13] This element, when released into the atmosphere, can cause an increase in the occurrence of acid rain.[14,15] Although chloride itself does not have negative effects on the environment, its presence in petroleum coke can impair coke quality for industrial use.[9,11,16] Thus, the determination of sulfate and chloride content in petroleum coke is essential to evaluate its appropriate use and its effect on the environment.

In samples of petroleum coke, chloride has been determined using inductively coupled plasma-optical emission spectrometry (ICP OES),[6,9] ion chromatography (IC)[11] and inductively coupled plasma mass spectrometry (ICP MS).[9] Sulfur has been also determined by ICP OES,[6] and using the method dictated in ASTM 5016.[17]

Techniques such as IC, ICP OES, and ICP MS, normally require the introduction of a dissolved sample. The fact that petroleum coke samples have a chemical resistance to acid oxidation, even when high temperatures and pressure are employed, complicates the sample preparation step.[6,10,11] Because the organic constituents of petroleum coke behave like fuel under a rich oxygen atmosphere, combustion techniques have been successfully used for petroleum coke digestion. When combustion is performed in closed vessels, as it is in microwave induced combustion (MIC), high sample masses can be digested, affording final digests with a low residual carbon content (RCC).[6,11] There is no

loss of volatile analytes, allowing the use of more dilute absorbing solutions, thus favoring the achievement of low limits of detection.

The detection techniques discussed above are relatively expensive, making the development of analytical procedures based on less costly methodologies important. Flow injection analysis (FIA) is considered a suitable method for handling sample and reagent solutions for analytical purposes, and provides the relatively high throughput necessary for routine analysis.[18-21] The FIA approach has already been employed to determine sulfate in plant digests by turbidimetry[22,23] and chloride in cement and water by spectrophotometry.[24,25]

In these cases, mercury thiocyanate and barium chloride are the reagents most commonly used. However, there are environmental restrictions to their use due to the environmental risks associated with the release of mercury and barium into the environment. According to green analytical chemistry guidelines (GAC),[26,27] if the use of an environmentally restricted reagent is inevitable, as little as possible should be used. This guideline is difficult to adhere, when the continuous pumping of reagent solutions, as is required for typical FIA systems, is employed.[22-24] However, the multicommuted flow analysis (MCFA) process may be a viable alternative. MFCA is a flow analysis approach in which sample and reagent solutions are inserted into the analytical path intermittently, allowing a significant reduction in reagent consumption and waste generation.[28-31]

The most important aspect of a flow analysis system is the fluid propulsion process, which is usually performed using a peristaltic pump.[32] Other fluid propelling devices, such as solenoid mini-pumps[33,34] and multisyringes,[35,36] have also been employed. While the peristaltic pump and solenoid mini-pump propel solutions forward, syringe pump operation comprises two alternating steps, one for solution loading and another for solution delivery. This working pattern has a potential limiting factor, but may be overcome by including solenoid valves in the manifold.[35-37] Syringe pumps have a relatively simple design that enables their construction without the need of sophisticated machining of components, thus making them cost-effective fluid propelling devices that can be constructed in a typical laboratory workshop.

In the present work, we have developed a multicommuted flow system for the simultaneous determination of sulfate and chloride in MIC digests of

petroleum coke. The flow analysis setup was designed to use a homemade syringe pump as the fluid propelling device.

Usually, the manifold base on the multisyringe approach has been designed to allow a sample aliquot to be inserted into a holding coil, which is subsequently displaced toward the detector by reverting the direction of the syringe piston displacement. The addition of reagent solutions to the sample zone is performed while the second step proceeds.[35,36,38,39] This configuration has been successfully employed for the determination of individual analytes. Intending to develop a procedure for the simultaneous determination of sulfate and chloride in MIC digests of coke samples, a flow system based on multicommuted flow analysis process,[40,41] was designed with two sampling loops instead of a holding coil. Control software was designed to perform the displacement of the syringe pistons, thus controlling the commutation of solenoid valves in order to load sampling loops with slugs of sample and reagents solution for each analyte. This arrangement allowed that reactions to produce the chemical species to be detected, begin while the sampling step proceeded, thus improving the sampling rate.

2. Experimental

2.1. Apparatus and accessories

The flow system module and the photometric detector comprised the following equipment setups and accessories: a motorized homemade syringe pump furnished with four 5.0 mL glass syringes, four three-way solenoid valves (HP225T031, NResearch) and an electronic interface controlled by a microcomputer; a flow analysis manifold comprising seven solenoid pinch valves (225P011-11, NResearch), and two polyethylene reactor coils (100 cm x 0.8 mm i.d.); Five-way (2 units) and three-way (5 units) flow line junctions machined in acrylic; a digital interface comprising two integrated circuits ULN2803, assembled as shown below; two similar photometers, each employing a 5 mm high-intensity emission LEDs with a maximum emission wavelength of 472 nm, two 0PT301 photodetectors (Texas Instruments), two glass flow cells with a 50 mm optical path length (1.2 mm i.d.), molded as described elsewhere,[42] two BC547 transistors and two variable resistors (5 kΩ);

a stabilized power supply of +12 V and -12 V (0.5 A) to power the photometers, and a stabilized power supply of 12 V (2.0 A) to feed the syringe pump and solenoid valves; a microcomputer equipped with a PCL711 electronic interface card (Advantech) and running a software written in Quick BASIC 4.5.

To allow accuracy assessment, an inductively coupled plasma optical spectrometer (PerkinElmer, Optime 4300 DV, EUA) with an axial view configuration was used for the determination of S (180.669 nm) and C (193.030 nm) for sulfate analysis, and a modular chromatographic system (Metrohm Ion Analysis, Herisau, Switzerland), was used for chloride determination.

2.2. Reagents and solutions

All solutions were prepared with purified water with an electric conductivity less than 0.1 μS cm^{-1}. All chemical reagents were of analytical grade.

A $8.5x10^{-3}$ mmol L^{-1} NH_4OH solution (Merk, Darmstadt, Germany) was prepared by diluting the concentrated reagent in water. A sulfate stock solution (1.000 g L^{-1}) was prepared by dissolving $(NH_4)_2SO_4$ (Merk) in water. Working standard solutions ranging from 10.0 to 700.0 mg L^{-1} of SO_4^{2-} were prepared by appropriate dilution of the stock solution with 50 mmol L^{-1} NH_4OH. A 10% (w/v) $BaCl_2.2H_2O$ solution (Merck) was prepared by dissolving the respective solid in a 0.1% (w/v) Tween 80 solution (Merck). A 0.4% (w/v) EDTA solution (Merck) was prepared by dissolving the solid in a 0.2 mol L^{-1} NaOH solution (Merck).

The chloride stock solution (1.000 g L^{-1}) was prepared by dissolving NaCl in water. Working standard solutions ranging from 0.06 to 10.00 mg L^{-1} of Cl^-, were prepared by dilution of the stock solution with 50 mmol L^{-1} NH_4OH. A 0.06% (w/v) $Hg(SCN)_2$ (Merck) plus 1% (w/v) $Fe(NO_3)_3.9H_2O$ (Merck) solution was prepared by dissolving the mercury compound in 15 mL absolute ethanol (Merck). A 1% (w/v) $Fe(NO_3)_3.9H_2O$ solution was prepared by dissolving 1.000 g of solid in 4 mL of a 5 mol L^{-1} HNO_3 solution. After dissolution, this was added to the mercury solution and the volume was made up to 100 mL with water.

2.3. Sample preparation

The petroleum coke samples were decomposed employing the microwave induced combustion (MIC) methodology,[6] using a microwave oven

(Multiwave 3000, Anton Paar, Graz, Austria) equipped with 8 quartz vessels (80 mL, maximum temperature and pressure of 280 ºC and 80 bar, respectively). After cryogenic milling and drying to constant mass, samples were pressed as pellets using a hydraulic press (15 ton, Specac, Orpington, UK) prior to MIC decomposition. Sample pellets (500 mg) were positioned in a quartz holder containing a disc of filter paper wetted with 50 µL of a 6 mol L^{-1} NH_4NO_3 (Merck), used as the igniter for MIC. The holder was positioned into a quartz tube with 6 mL of 50 mmol L^{-1} NH_4OH (Merck), used as the absorbing solution to retain Cl and S compounds after combustion. Each vessel was pressurized with 20 bar of oxygen (99.6%, White Martins-Praxair, Brazil) before microwave heating at 1400 W for 5 min (1 min for sample combustion plus 4 min as a reflux step), followed by a cooling step (20 min). After the digestion procedure, all digests were diluted with water to 50 mL for further analyte determination.

The accuracy of the MIC digestion procedure was evaluated by using certified reference material (CRM). Sulfate was determined in a CRM of petroleum coke (NIST 2718, Green Petroleum Coke, National Institute of Standards & Technology, USA), while chloride was determined in a CRM of coking coal (BCR 181, Coking Coal, Institute for Reference Materials and Measurements, Belgium).

2.4. Photometer description

The diagram of the photometers is shown in Fig. 1, and shows that the photometers were designed to be identical, but with independent working conditions. The intensity of the radiation emitted by LED_1 and LED_2 is a function of the electric current intensity flowing through them, controlled by the variable resistors (5 kΩ) coupled to the bases of the transistors (Tr_1 and Tr_2). The radiation beams I_1 and I_3 emitted by LED_1 and LED_2 propagate through the flow cells fc_1 and fc_2, respectively.

The radiation beams I_2 and I_4 are directed by the glass cylinders (gl) towards the photodetectors Det_1 and Det_2, respectively, generating electric potential differences (mV) directly related to the intensity of the respective radiation beam. When a flow cell is filled with a solution that absorbs radiation in the same wavelength range as that emitted by the LED, absorption occurs during the propagation of the radiation through the flow cell, causing an

attenuation of the radiation beam intensity. As a result, the radiation beams (I_2 and I_4) reaching the detectors is less intense ($I_1 > I_2$ and $I_3 > I_4$).

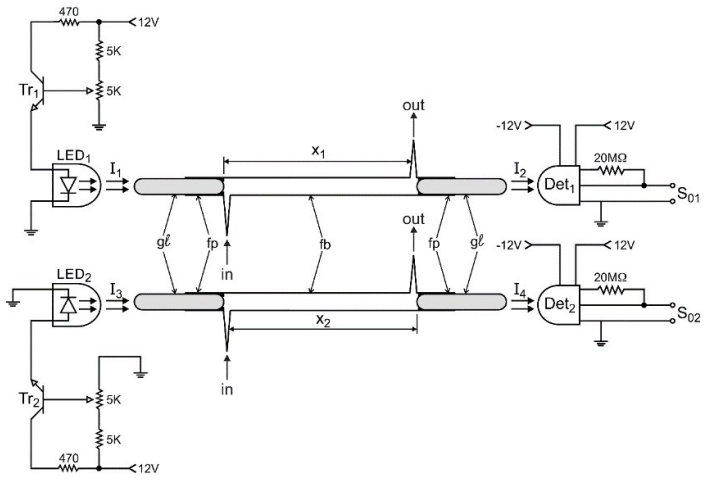

Figure 1. Diagram of the photometers. Tr_1 and Tr_2 = transistor BC547; LED_1 and LED_2 = light emitting diode, λ = 472 nm; fb = flow cell body, glass tube (boron-silicate); x_1 e x_2 = 50 mm long and 1.2 mm internal diameter; gl = glass cylinders; fp = fused point; I_1, I_2, I_3, and I_4 = radiation beams emitted by the LEDs entering and exiting the flow cell, respectively; Det_1 and Det_2 = photodetector 0PT301; in and out = fluid input and output, respectively; So_1 and So_2 = signal generated by the photometers (mV).

The variation of intensity is a function of the concentrations of chemical species in the flow cells. Under these conditions, the electric potential difference generated by each photometer is lower than that when the flow cell is filled with water. This phenomenon was exploited to obtain absorbance values for use in the determination of analyte concentrations.

2.5. Description of reactions and flow analysis module

The procedure for chloride determination is based on the displacement reaction of thiocyanate from mercury/thiocyanate compound by chloride ions, followed by the reaction of the liberated thiocyanate with iron(III), forming a colored complex which may be monitored by spectrophotometry.[38,39] The maximum of the absorption band can vary from 460 to 490 nm, depending on the reacting medium.[43] In the current work, the photometric detection was

performed using a blue LED with a maximum emission at 472 nm and a bandwidth of 25 nm.

The procedure for sulfate determination is based on its reaction with barium ions to form a suspension,[23] which causes light scattering in the flow cell, thus decreasing the intensity of the radiation beam. This effect is exploited in the current work with analytical proposal. Over time, accumulation of the barium sulfate precipitate in the flow cell can cause baseline drift. This drawback has been overcome by implementing a cleaning step using an alkaline EDTA solution to dissolve the barium sulfate precipitate,[23] deployed using the flow system manifold shown in Fig. 2.

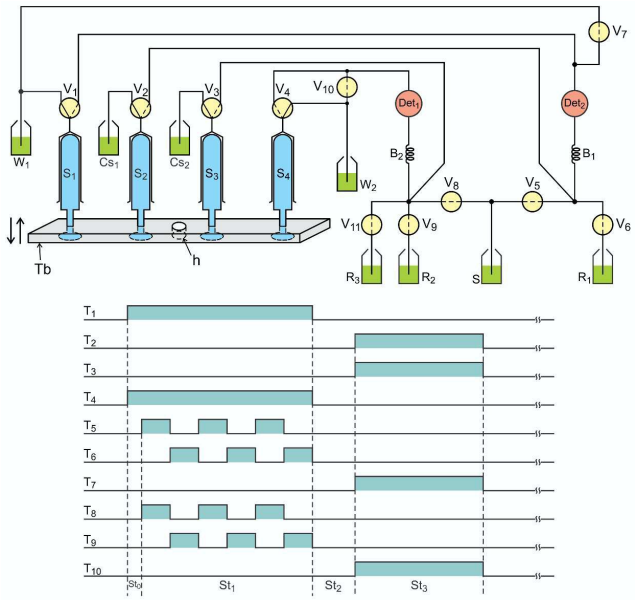

Figure 2. Diagram of the flow system manifold. Tb = traction plate of aluminum, h = threaded hole (female) to attach the displacing screw (not shown); S_1, S_2, S_3 and S_4 = syringes; V_1, V_2, V_3 and V_4 = three way solenoid valve; V_5, V_6,…V_{11} = pinch solenoid valves; S = sample; R_1 = mercuric thiocyanate solution; R_2 = barium chloride solution; R_3 = EDTA solution; Cs_1, Cs_2 = carrier solutions (nitric acid 0.014 mol L^{-1} and water respectively; B_1, B_2 = reaction coil, 100 cm long and 0.8 mm inner diameter; Det_1, Det_2 = photometer, λ = 472 nm; W_1, W_2 = waste; T_1, T_2, ... T_{10} = drive the timing diagram valves V_1, V_2, ...V_{10}, respectively. Dashed and solid lines in the valve symbols V_1, V_2, V_3 and V_4 indicated the fluid pathway when the valves were switched on or off, respectively. Dashed lines in the valve symbols V_5, V_6 ... V_{11} indicate that are normally closed, therefore permit fluid flow only when they are connected.

The flow system setup depicted in Fig. 2 is designed to use an automatic syringe pump for fluid propulsion. The displacement of the syringe pistons forward and backward is performed using the direct current motor of the syringe module, which is coupled to the traction plate (Tb, Fig. 2) using a screw attached to motor shaft.

The section of the manifold comprising syringes S_3 and S_4, solenoid valves V_3, V_4, V_9, V_{10}, and V_{11}, reaction coil B_1, and Det_2 is designed to process the sample for sulfate determination. The section comprising the other devices is for chloride determination.

The interfaces used to drive the syringe pump and the solenoid valves are shown in Fig. 3.

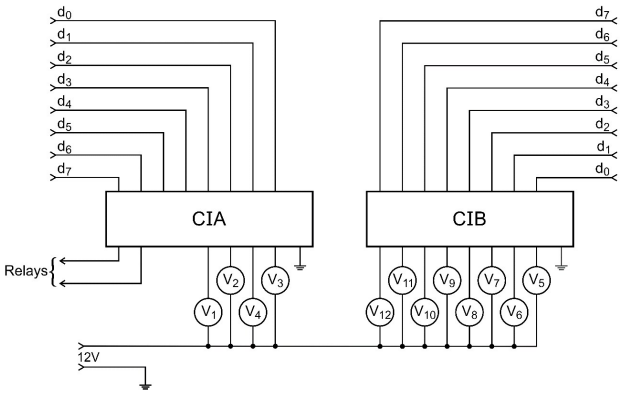

Figure 3. Diagram of the control interface. CIA and CIB = integrate circuit ULN2803; V_1, V_2, V_3 and V_4 = three-way solenoid valves; V_5, V_6, ….., V_{12} = solenoid pinch valves normally closed, d_0, d_1, …..d_7 = control lines from the PCL 711 interface card.

The section assigned as CIA is used to drive the syringe motor and solenoid valves V_1, V_2, V_3, and V_4, which are used to load the syringes with solutions and to direct them toward the flow system. The section assigned as CIB is used to drive the solenoid valves V_5 to $V_{11,}$ which comprises the flow system manifold depicted in Fig. 2.

In the configuration shown in Fig. 2, the syringes are in the empty position. When the control software is run, the microcomputer recognizes this position, using the PCL711 card to read a signal generated by the syringe pump. Subsequently, the microcomputer sends a control signal (bits d_7, d_6)

through the PCL711 interface to activate the syringe pump in order to displace the syringe piston down, maintaining solenoid valves V_1, V_2, V_3, and V_4 in the off position, thus aspirating the solutions to fill each syringe. When the syringe piston reaches maximum displacement, the pump motor automatically switches off and a busy signal is generated to be detected by the microcomputer.

The solenoid valves V_1, V_2, V_3, and V_4 coupled to the syringes are used to select the way to displace solutions, while moving the syringe pistons either upward (forward) or downward (backward). These actions are performed by controlling the direction of rotation (right or left) of the syringe pump motor.

The manifold which handles the sample and reagent solutions comprises the solenoid valves V_5 to V_{11}, which work as depicted in the time switching diagram (T_1, T_2, ... T_{10}). Prior to a sampling run, the syringe pump motor is used to displace the syringe pistons down. In the first step (st_1), the solenoid valves V_1 and V_4 are switched on, while valves V_5, V_6, V_8, and V_9 are switched on/off three times. As we can see, valves V_5 and V_8 are switched on at the same time, followed by a switching on of valves V_8 and V_9, and so on. This sequence loads reaction coil B_1 with a string of slugs of the sample solution in tandem with slugs of the reagent solution R_1. A similar sequence loads reaction coil B_2 with slugs of sample and reagent solution R_2. Subsequently, the pump motor is activated to displace the syringe piston up. After a delay time of 2.0 s to stabilize flow rate, valves V_2 and V_3 are switched on. When this happens, the CS_1 and CS_2 solutions flow through valves V_2, V_3, V_7, and V_{10} towards reaction coils B_1 and B_2, respectively. In this configuration, the sample zone containing the reagent for chloride is displaced through the flow cell of the photometer (Det_2), which generates a signal related to chloride concentration. Simultaneously, a similar situation occurs with the CS_2 stream, allowing the monitoring of the signal related to sulfate concentration generated by the photometer (Det_1).

This set of actions comprises an analytical run, which can be repeated the number of times established by the control software. At the end of the number of runs established, a cleaning step is applied to the sulfate manifold (reaction coil B_2 and flow cell of the photometer Det_1) by aspirating an aliquot of EDTA solution through them. This step is performed by switching on valves V_4 and V_{11} for a time interval of 5 s. Following this, valves V_3 and V_{10} are switched

on for 7 s in order to wash the manifold with the carrier solution (Cs_2). To perform the cleaning step, the syringe module is activated to displace the piston upward. The set of actions described above is depicted in Table 1.

Table 1. Sequence of events.

Step	Event	Rotation	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9	V_{10}	V_{11}	time/s
1	Reagent fill channel	L	1	0	0	1	0	1	0	0	1	0	1	4.0
2	Channels filling	L	0	0	0	0	0	0	0	0	0	0	0	10
3	Washing analytical path	R	0	1	1	0	0	0	1	0	0	1	0	14
4	Photometer calibration	S	0	0	0	0	0	0	0	0	0	0	0	-
5	Cleaning with EDTA	L	0	0	0	1	0	0	0	0	0	0	1	5.0
6	Cleaning with EDTA	R	0	0	1	0	0	0	0	0	0	1	0	7.0
7	Filling flow lines with sample	L	1	0	0	1	1	0	0	1	0	0	0	3.0
8	Washing sample channel	R	0	1	1	0	0	0	1	0	0	1	0	3.0
9	Sampling for chloride[a]	L	1	0	0	0	1	0	0	0	0	0	0	1.0
	Sampling for chloride[a]	L	1	0	0	0	0	1	0	0	0	0	0	0.5
10	Sampling for sulfate[b]	L	0	0	0	1	0	0	0	1	0	0	0	0.5
	Sampling for sulfate[b]	L	0	0	0	1	0	0	0	0	1	0	0	1.0
11	Signals reading chloride/sulfate	R	0	1	1	0	0	0	1	0	0	1	0	6.0

The events labelled as *a*and *b* correspond to the sampling cycles for chloride and sulfate, respectively. L, R, and S in the rotation column = motor rotation direction for left, right and stop, respectively. V_1 – V_{11} = solenoid valves as described in Fig. 2. Numbers 0 and 1 indicate that related valve is switched off or on, respectively. The numbers in the last column are the selected time intervals.

When the program is running, the software queries whether a photometer calibration should be performed. If affirmative, the microcomputer sends control signals to the syringe module to displace the syringe pistons upward and to switch on valves V_2, V_3, V_7, and V_{10}. When this happens, the Cs_1 and Cs_2 fluids flow through the flow cells of both photometers in order to fill them with the carrier solutions. The signals generated by the photometers termed here as full-scale measurements (Fsm_1, Fsm_2) are adjusted to 2000 mV using the variable resistors wired to the base transistors Tr_1 and Tr_2 (Fig. 1). Afterwards, measurements related to diffuse radiation (Dfm_1 and Dfm_2) are achieved by aspirating a highly colored solution through both flow cells. These solutions are prepared by mixing 15 mL of a 4% (w/v) SCN^- solution with equal volumes of standard Fe(III) solutions with concentrations of 40 and 50 mg L^{-1},

respectively. The measurements Dfm_1 and Fsm_1, and Dfm_2 and Fsm_2, related to the Det_1 and Det_2 photometers, are saved to be used in absorbance calculations.

The calibration step to adjust the full-scale measurements is performed 15 min after powering on the photometer, while assays to achieve diffuse measurements are performed once a week, since maintaining the full scale measurements at 2000 mV does not significantly affect their variation. The steps from 5 to 8 are carried out once prior to beginning the analysis of a new sample.

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This flow system was designed to handle sample and reagent solutions based on the multicommuted process. Therefore, the volumes of sample and reagent solutions inserted into the manifold are a function of the pumping flow rate and the time for which the selected valve is switched on. Because the pumping flow rate was constant throughout, the time intervals and concentration of the reagent solutions were the variables studied.

3. Results and discussion

3.1. General comments

The method for the photometric determination of chloride based on the displacement reaction of thiocyanate from mercury/thiocyanate compound by chloride ions was proposed in the 50's, and has become an alternative to classical methods, such as the Vollhard and Mohr methods.[43] This method has a high sensitivity and fast reaction time, allowing the design of high-throughput flow systems for chloride determination. Furthermore, there is no interference from other chemical species, so it has become the preferred method for chloride determination by spectrophotometry.[24,25,31,38,39] On a smaller scale, procedures

for the determination of chloride have been proposed based on reaction with silver nitrate to form a precipitate that may be detected by turbidimetry,[45,46] or by reaction with silver chloranilate, allowing detection by spectrophotometry.[47,48] In the former case, the procedure has low sensitivity and low sampling rate. In the latter, a column filled with solid silver chloranilate (Ag_2Ch) is coupled to the flow system manifold, and interference caused by concomitant chemical species is eliminated by means of an ion exchange resin column attached in tandem with the silver chloranilate column. However, this requirement is difficult to implement in a flow system for simultaneous determination. For these reasons, the method based on reaction with Hg^{2+} was selected. The flow system manifold was designed to work with a reduced volume of reagent, as suggested by AGC guidelines.[26,27]

3.2. Evaluation of the MIC procedure for Cl^- and SO_4^{2-} determination using MCFA

Digestion efficiency is a critical parameter in analyses performed by the FIA system. A great deal of interference can be observed if a high amount of dissolved organic carbon is still present in the final digests. Thus, digestion efficiency was evaluated by carbon determination using ICP OES. The results obtained were expressed as RCC, which was always lower than 1% (< 5 mg L^{-1}) when petroleum coke was digested by MIC. This indicates a high digestion efficiency, and ensures a determination step almost completely free from interference due to the presence of carbon in the final digests.

The proposed determination system is also dependent on the analyte species present in the absorbing solution obtained from MIC. For this reason, we evaluated the oxidation state of the analyte present in the final solution, as it could negatively impact the detection based on reactions of Cl^- and SO_4^{2-}. First, the presence of Cl and S species were determined employing ion exchange chromatography, the results of which are shown in Fig. 4.

Analyzing the read-out displayed in Fig. 4, we observe that only signals related to the retention times of Cl^- and SO_4^{2-} are recorded. Species in other oxidation states, such as ClO^{3-} and SO_3^{2-}, that might cause interference during the detection step, were not observed in the chromatogram. Therefore, samples

prepared using MIC were considered suitable for further analysis employing the proposed MCFA procedures.

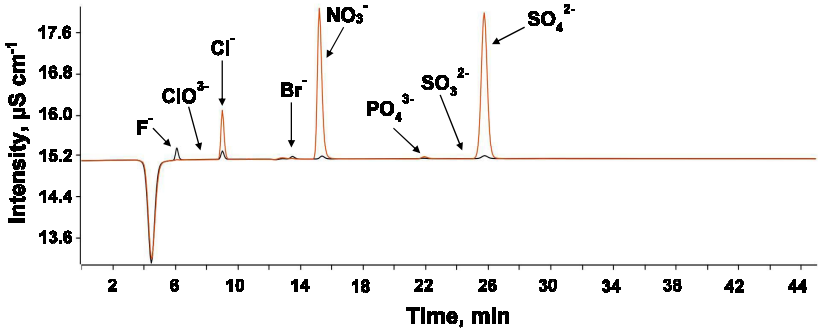

Figure 4. Chromatogram record of a coke sample after digestion by MIC. Black line represents the retention time obtained from standard solution. Red line represents the retention time obtained from sample after MIC digestion.

3.3. Parameters for sulfate determination

3.3.1. Effects of the sample zone volume

Because the volume of the sample zone can affect the sensitivity of the procedure, assays were performed in order to find the optimal volume. Assays were performed using time intervals of 0.5 and 1.0 s for the sample and barium chloride solution, respectively, and varying the number of sampling cycles (Table 1). These experiments yielded the results shown in Fig. 5. These results show that the signal increases with the volume of the sample zone up to 2100 µL, while for a volume of 2400 µL no significant increase in the signal is observed. This effect is normal for a flow system. The volume of the sample zone can be selected within this volume range in order to achieve the required analytical result. However, it is important to consider that a large sample volume can improve sensitivity, but will impair the sampling throughput.

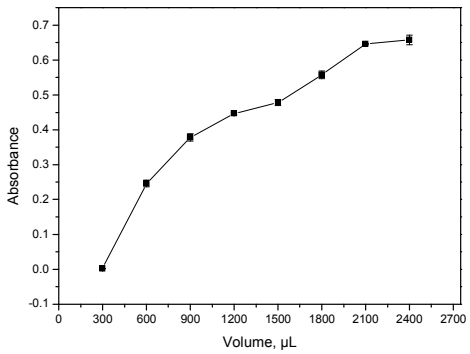

Figure 5. Effect of the sample zone volume. Assay carried out using a 50 mgL^{-1} sulphate and flow rate of 200 μLs^{-1}.

3.3.2. Effect of reagent volume

With the reagent concentration being kept constant, the optimum amount available for the reaction was investigated as a function of the volume inserted while performing the sampling step. In order to find the optimum signal response, we experimented with keeping the solenoid valve V_9 on for time intervals of 0.25, 0.5, 1.0, 1.5, and 2.0 s (Fig. 2) and applied five sampling cycles. Under these conditions, the volume of reagent solution per sampling cycle varied from 50 to 400 µL, while the volume of the sample slug was 200 µL. No significant variation in the magnitude of the signals is observed for the time intervals ranging from 0.5 to 1.5 s. However, a decrease in signal magnitude was observed with a time interval of 2.0 s. In this case, there could have been a dispersion effect due to the volume of the reagent solution aliquot, which was twice the volume of the sample aliquot. Considering these results, we selected a time interval of 1.0 s for subsequent evaluations.

3.3.3. Photometer response for sulfate determination

The analytical procedure was based on light scattering caused by the barium sulfate suspension produced. Absorbance is generally employed as the parameter to achieve sulfate concentration. Spectrophotometers equipped with an optical system typically emit a radiation beam with a narrow wavelength band, tending to be parallel. However, in the present work we employed a

homemade photometer using an LED as the radiation source, which provided a radiation beam that was neither monochromatic nor parallel. Since these features would impair the range of linear responses, we implemented a set of assays to establish the best absorbance range to be used when using a LED based photometer. The signal generated by the flow system presented a transient signal profile related to analyte concentration, as shown in Fig. 6.

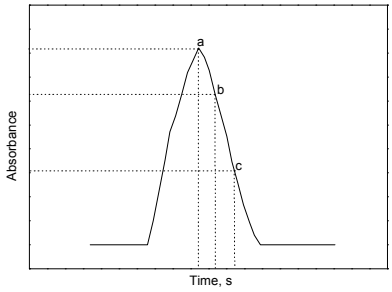

Figure 6. Record of the transient signal. Record referred to 200 mgL^{-1} sulphate standard solution and settling three sampling cycles. Other parameters as described before.

Usually, the value of the peak height was used as the measurement parameter. Each point on the resultant profiles is associated with an instantaneous analyte concentration. This feature has been exploited previously to perform on-line dilution.[49,50] In the present work, it was used to determine the range where absorbance could be used as the parameter for sulfate determination. Since each point on the signal profile represents an analyte concentration, data acquisition was programed to use an increased delay time before the signal monitoring began. The evaluations were performed using sulfate standard solutions with concentrations ranging from 50 to 700 mg L^{-1}. Taking into account the maximum value of the signal as a measurement parameter, and applying a linear regression methodology, we achieved the results shown in Table 2.

The results shown in the first row of Table 2 are related to the measurements carried out without a delay time ($\Delta t = 0$), thus the maximum peak height was achieved by monitoring the whole sample zone. The results, including absorbance range, shown in the second and third rows are similar to that of the first. When the delay times are set at 6.0 and 8.0 s, the absorbance

range narrows and its magnitude is reduced significantly. This indicates that the signal reading step begins at the falling edge of the signal profile (Fig. 6). Nevertheless, an improvement in linearity is observed. As we can see, similar results are achieved when three sampling cycles are used. In this case, the volume of the sample zone is increased by 50%, which serves to widen the absorbance range, but no improvement in linearity is observed. However, when the delay time is 6.0 and 8.0 s, the absorbance ranges are similar to those observed for two sampling cycles.

The results shown in the first row of Table 2 are related to the measurements carried out without a delay time ($\Delta t = 0$), thus the maximum peak height was achieved by monitoring the whole sample zone.

Table 2. Photometer response as function of delay time

Sampling cycles	Δt(s)*	Intercept	Slope	R	Absorbance range
2.0	0	0.2083	0.0019	0.9771	0.2421 – 1.4585
	2.0	0.2017	0.0019	0.9772	0.2368 – 1.4349
	4.0	0.1951	0.0019	0.9806	0.2226 – 1.4157
	6.0	0.0590	0.0014	0.9943	0.1024 – 1.0102
	8.0	0.0369	0.0006	0.9983	0.0707 – 0.5235
3.0	0	0.3820	0.0026	0.9609	0.4158 – 1.9890
	2.0	0.3761	0.0026	0.9676	0.4150 – 2.0316
	4.0	0.3680	0.0025	0.9633	0.4037 – 1.8886
	6.0	0.1540	0.0014	0.9933	0.2076 – 1.0927
	8.0	0.0064	0.0008	0.9933	0.0553 – 0.6051

*Delay time before beginning the signal reading step.

The results, including absorbance range, shown in the second and third rows are similar to that of the first. When the delay times are set at 6.0 and 8.0 s, the absorbance range narrows and its magnitude is reduced significantly. This indicates that the signal reading step begins at the falling edge of the signal profile (Fig. 6). Nevertheless, an improvement in linearity is observed.

As we can see, similar results are achieved when three sampling cycles are used. In this case, the volume of the sample zone is increased by 50%, which serves to widen the absorbance range, but no improvement in linearity is observed. However, when the delay time is 6.0 and 8.0 s, the absorbance ranges are similar to those observed for two sampling cycles.

The results shown in Table 2 show that samples within a wide concentration range can be processed employing a delay time of 6.0 or 8.0 s. The linear responses achieved for both time intervals are better than those reported in previous papers.[22,23] Analyzing the linear relationship of the results shown in Table 2, we observe that an absorbance value of around 1.0 is a limiting value of the proposed setup, when light scattering by suspension of particles was associated with the analyte concentration.

Based on these results, we decided that the optimum conditions for our system are: three sampling cycles, time intervals of 0.5 and 1.0 s for the insertion of sample and reagent solutions, respectively, and a delay time of 6.0 s before beginning the signal reading step. To find the overall response of the proposed system, a set of sulfate standard solutions at concentrations of 10, 25, 50, 100, 150, 200, 300, 400, 500, 600, and 700 mg L^{-1} was processed. The maximum peak height was chosen as the measuring parameter, giving the following linear relationship: absorbance = 0.0554 + 0.0013 mg L^{-1} C (r = 0.9994). This sulfate concentration range is wider than those presented in previous papers.[22,23,42] This could be considered as a useful advantage, allowing analysis of samples with a wide concentration range without any change in the flow system structure or working pattern.

3.3.4 Effect of EDTA as a cleaning solution

The barium sulfate suspension tended to adhere to the inner wall of the reaction coil, causing baseline drift and eventually can clog it. To overcome this drawback, a cleaning step using an EDTA solution in alkaline medium was implemented, as described in the experimental section. The assay was performed using EDTA solutions with concentrations of 0.05, 0.1, 0.2, 0.4, and 0.6% (w/v) prepared in a 0.2 mol L^{-1} NaOH solution and an 800 mg L^{-1} sulfate standard solution. When EDTA solutions with concentrations of 0.2, 0.4 and

0.6% (w/v) were pumped through the reaction and flow cell for 5.0 s, no base line drift was observed. Thus, a 0.4% EDTA solution was selected for subsequent evaluations.

3.4. Parameters for chloride determination

3.4.1. Effect of sample volume

Considering that the sample volume can affect the magnitude of the analytical signal, we evaluated the appropriate volume to be used. The assay was performed with solenoid valve V_1 switched on (Fig. 2) while the syringe pistons were forced down. At the same time, solenoid valves V_5 and V_6 were switched on/off alternately three-times (three sampling cycles). Valve V_6 was kept switched on for 0.5 s, while the time interval for solenoid valve V_5 was varied from 0.5 to 2.5 s. Under these conditions, the volumes of sample slugs were varied from 100 to 500 µL. The results show an increase of up to 20% when the slug volume increased from 100 to 200 µL. Since identical values for higher volumes were obtained, a time interval of 1.0 s was selected.

3.4.2 Effect of the reagent solution volume

Mercury thiocyanate was prepared as a saturated solution, thus the establishment of the best conditions for the reaction involved the variation of solution volume only. The time intervals for the switching on/off of solenoid valve V_2 (Fig. 2) were varied from 0.13 to 1.00 s, at increments of 0.25 s. The assays were performed using a 10.0 mg L^{-1} chloride standard solution and three sampling cycles. With an aspiration flow rate of syringe S_1 at 200 µLs^{-1}, the volume of the reagent solution slugs was varied between 25 and 200 µL. The results show a small increment in signal when the slug volume increases from 25 to 50 µL, and a tendency for constant values at higher volumes. Based on these results, a time interval of 0.5 s was selected for additional experiments.

3.5. Simultaneous determination of sulfate and chloride

The assays discussed above were performed to find the appropriate operational conditions for both analytes. The selected values of the variables studied are summarized in Table 3.

Table 3. Selected values of the studied variables

	Chloride		Sulfate	
Parameter	Studied range	Chosen	Studied range	Chosen
Sample insertion time (s)	0.5 – 2.5	1.0	0.25 – 2.0	0.5
Reagent insertion time (s)	0.125 – 1.0	0.5	0.25 – 2.0	1.0
Sampling cycles	2 – 10	3	1 – 5	3

The evaluations previously discussed were carried out individually for each analyte. This section discusses the results achieved when running the flow system (Fig. 2) for simultaneous determination, yielding the results shown in Fig. 7. The uniformity of the results indicates the excellent performance of the proposed setup. The curves shown in Fig. 7a and 7b show that, for both analytes, a wide range of linear responses was achieved.

We compared the performance of our system with other existing analytical procedures for the determination of chloride and sulphate in water samples. Because samples of petroleum coke digested using MIC can be considered similar to a water sample, several papers which measured chloride and sulfate in aqueous samples were selected as references for comarison.[31,38,51,52] The parameters employed to evaluate the features of the analytical procedures used in these works are summarized in Table 4.

Analyzing the results of the proposed procedure in terms of sulfate determination we observe that, overall, they are favorable to the proposed procedure. The reagent consumption is higher than that in Ref. 51, but the linear range of our proposed procedures is wider, which is an advantage for large scale routine analysis.

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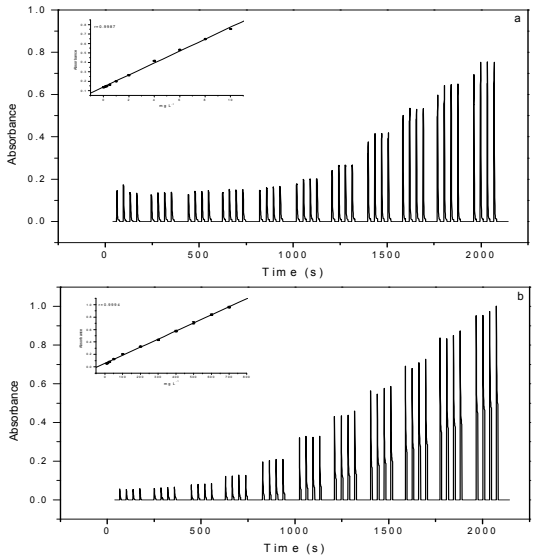

Figure 7. Records of the transient signals generated simultaneously. The set of record labeled as *a* correspond to chloride standard solutions of 0.0, 0.06, 0.125, 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0 mg L^{-1}, while the other one labelled as *b* is related with sulphate standard solutions of 10, 15, 25, 50, 100, 200, 300, 400, 500, 600, 700 mg L^{-1}.

Analyzing the results of the proposed procedure in terms of sulfate determination we observe that, overall, they are favorable to the proposed procedure. The reagent consumption is higher than that in Ref. 51, but the linear range of our proposed procedures is wider, which is an advantage for large scale routine analysis.

The results in terms of chloride determination show that the reagent consumption of the procedure reported in Ref. 30, is lower than that of the proposed procedure, but the volume of waste generated containing mercury is twofold. The others parameters are similar, except for the sampling rate for individual chloride determinations, which is 75 determinations per hour for the proposed procedure. However, an equal number of sulfate determinations are possible.

Table 4. Performance comparison

Parameters	Proposed procedure	Ref. 51	Ref. 52	Proposed procedure	Ref. 31	Ref. 38
	(SO_4^{2-})	(SO_4^{2-})	(SO_4^{2-})	(Cl^-)	(Cl^-)	(Cl^-)
Linear range (mg L^{-1})	10 - 700	20 - 200	10- 100	0.25 -10	1 - 10	1 - 40
Linear coef. (r)	0.9986	0.999	0.999	0.9994	0.996	0.999
Detection limit (mg L^{-1})	5.3	3.0	10.0	0.16	0.4	0.2
Reagent consumption (mg L^{-1})	20[a]	5.0[a]	22[a]	0.12[b]	0.1[b]	0.05[b]
Coefficient of variation (%)	3.0	2.4	1.6	0.9	2.3	0.8
Waste (mL)[c]	3.0	6.4	7.8	2.5	3.0	5.9
Sampling rate (h^{-1})	75	30	20	75	50	130

The labels *a* and *b* correspond to the consumption of barium and mercury per determination, respectively, while *c* indicates the volume of waste generated per determination.

3.5. Simultaneous determination of sulfate and chloride

In order to verify the effectiveness of the proposed MCFA system for simultaneous determination of sulfate and chloride, we analyzed digested samples of petroleum coke. Under the optimized conditions, six samples of petroleum coke were analyzed. The results obtained are presented in Table 5. For comparison, the samples were also analyzed using IC for chloride and ICP OES for sulfate (as total S). Both results are also presented in Table 5. Applying the paired *t*-test at a 95% confidence level, we obtained values of t_{tcal}= 0.30 and t_{tcal} = 0.32 for chloride and sulfate, respectively. The tabulated value for this

confidence level is t_{tab} = 2.57, indicating that, for both analytes, there is no significant difference between the results.

Table 5. Result comparison of chloride and sulfate in petroleum coke.

	Chloride		Sulfate	
Sample	Proposed procedure mg L^{-1}	Reference method (IC) mg L^{-1}	Proposed procedure mg L^{-1}	Reference method (ICP-OES) mg L^{-1}
1	0.345 ± 0. 020	0.372 ± 0.024	354.1 ± 2.5	349. 5 ± 1.7
2	0.424 ± 0.020	0.462 ± 0.019	341.9 ± 2.0	331.6 ± 2.3
3	0.640 ± 0.070	0.487 ± 0.022	337.6 ± 4.1	336.1 ± 3.7
4	0.425 ± 0.005	0.512 ± 0.013	331.9 ± 4.4	335.6 ± 2.0
5	0.229 ± 0.040	0.402 ± 0.018	338.1 ± 5.0	339.6 ± 0.6
6	0.510 ± 0.050	0.428 ± 0.030	341.1 ± 4.6	346.1 ± 4.4

Results are the average of three consecutive measurements

4. Conclusion

Our proposed MCFA system was used for chloride and sulfate determination in samples of petroleum coke prepared using digestion by MIC methodology. The results of these experiments clearly indicated that the system presents a convenient and efficient method, capable of high sampling throughput and a wide analytical range.

Additionally, the high digestion efficiency obtained using MIC, combined with the possibility of using diluted absorbing solutions, makes reagent coupling an easy and effective method for sulfate and chloride determination, even for samples which are hard to dissolve, such as petroleum coke.

The robustness of the proposed prototype system of syringes pump, and photometers is evinced by the fact that the setup operated for six months without requiring the replacement of a single component. The configuration of the flow system manifold allowed a sampling throughput higher than that usually attained employing a syringe pump as the fluid propelling device.[35,36,39] Furthermore, the effective concentration range of our system was shown to be wider than those reported for methods presented in earlier works.[22,23,31,32]

The proposed setup, and the optimized analytical procedure developed with it, combine favorable features, making our proposed methodology a cost-

effective alternative for sulfate and chloride determination in samples of petroleum coke. Its low volume of waste generation is a particularly useful feature considering the current importance of environmental sustainability.

Acknowledgements

The authors acknowledge financial support from FAPESP (process 2013/05728-2; 2011/23498-9) CNPq, CAPES, and INCTAA.

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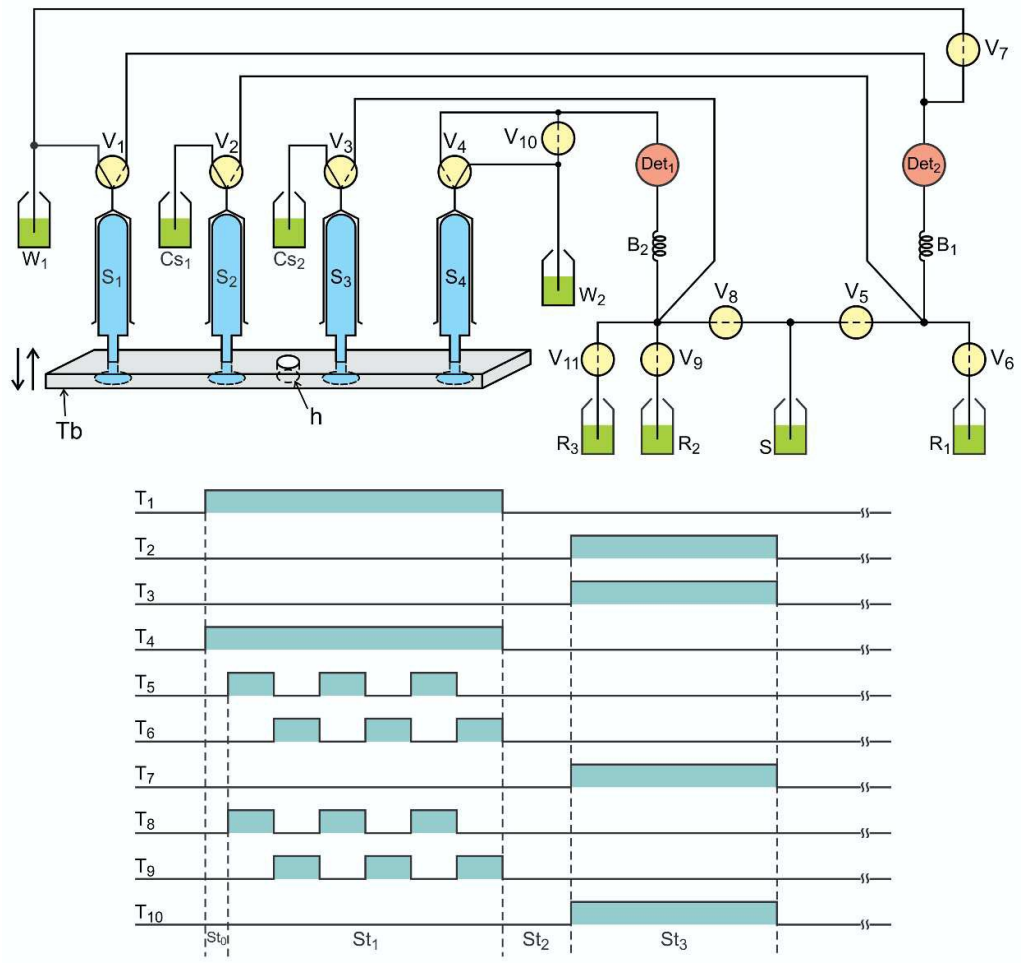

Diagram of the flow system and its working pattern

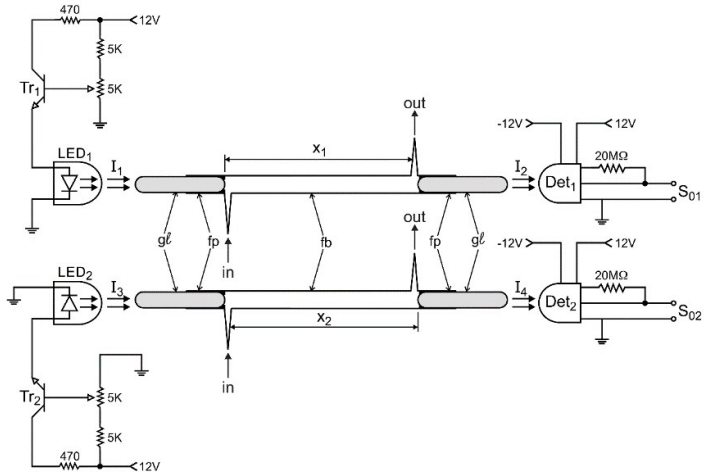

Figure 1. Diagram of the photometers. Tr_1 and Tr_2 = transistor BC547; LED_1 and LED_2 = light emitting diode, λ = 472 nm; fb = flow cell body, glass tube (boron-silicate); x_1 e x_2 = 50 mm long and 1.2 mm internal diameter; gl = glass cylinders; fp = fused point; I_1, I_2, I_3, and I_4 = radiation beams emitted by the LEDs entering and exiting the flow cell, respectively; Det_1 and Det_2 = photodetector 0PT301; in and out = fluid input and output, respectively; So_1 and So_2 = signal generated by the photometers (mV).

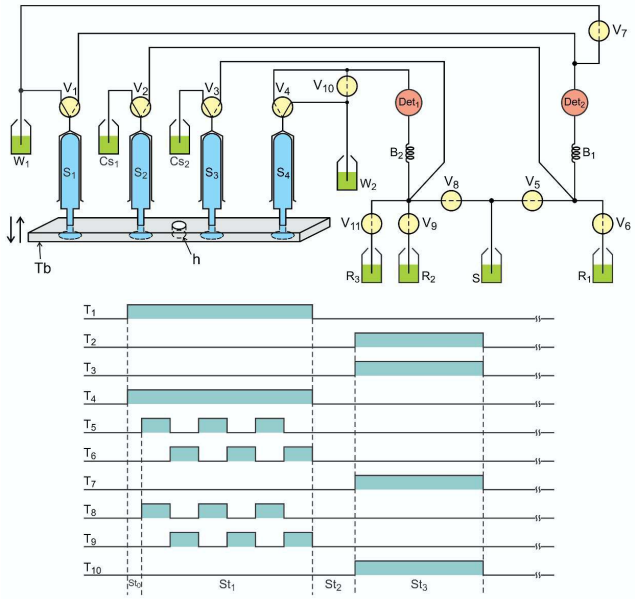

Figure 2. Diagram of the flow system manifold. Tb = traction plate of aluminum, h = threaded hole (female) to attach the displacing screw (not shown); S_1, S_2, S_3 and S_4 = syringes; V_1, V_2, V_3 and V_4 = three way solenoid valve; V_5, V_6,…V_{11} = pinch solenoid valves; S = sample; R_1 = mercuric thiocyanate solution; R_2 = barium chloride solution; R_3 = EDTA solution; Cs_1, Cs_2 = carrier solutions (nitric acid 0.014 mol L^{-1} and water respectively; B_1, B_2 = reaction coil, 100 cm long and 0.8 mm inner diameter; Det_1, Det_2 = photometer, λ = 472 nm; W_1, W_2 = waste; T_1, T_2, ... T_{10} = drive the timing diagram valves V_1, V_2, ...V_{10}, respectively. Dashed and solid lines in the valve symbols V_1, V_2, V_3 and V_4 indicated the fluid pathway when the valves were switched on or off, respectively. Dashed lines in the valve symbols V_5, V_6 ... V_{11} indicate that are normally closed, therefore permit fluid flow only when they are connected.

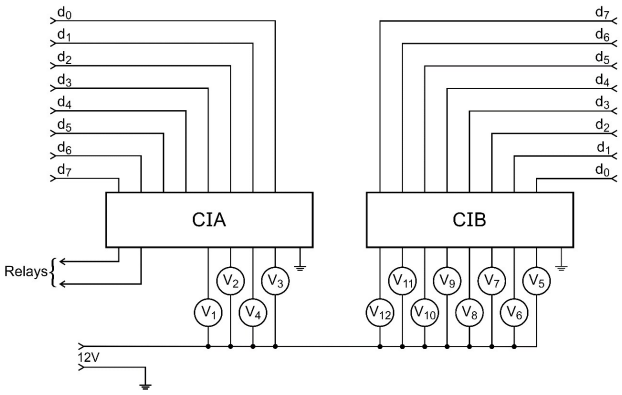

Figure 3. Diagram of the control interface. CIA and CIB = integrate circuit ULN2803; V_1, V_2, V_3 and V_4 = three-way solenoid valves; V_5, V_6, ….., V_{12} = solenoid pinch valves normally closed, d_0, d_1, …..d_7 = control lines from the PCL 711 interface card.

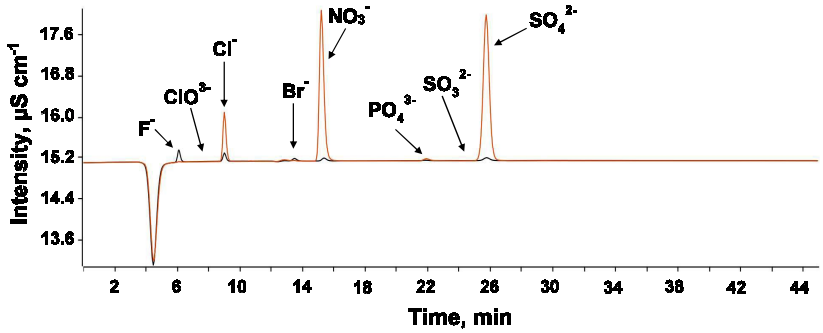

Figure 4. Chromatogram record of a coke sample after digestion by MIC. Black line represents the retention time obtained from standard solution. Red line represents the retention time obtained from sample after MIC digestion.

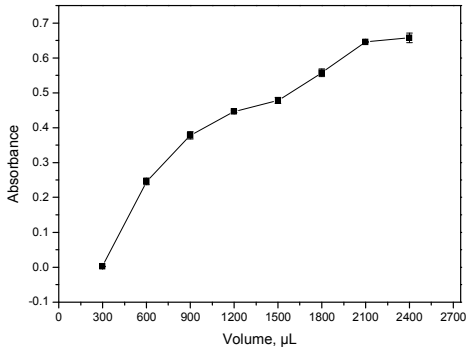

Figure 5. Effect of the sample zone volume. Assay carried out using a 50 mgL^{-1} sulphate and flow rate of 200 μLs^{-1}.

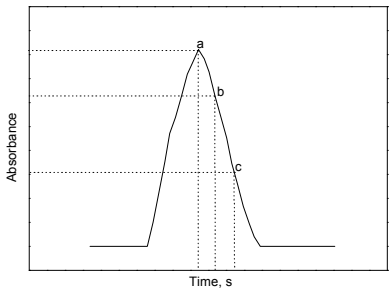

Figure 6. Record of the transient signal. Record referred to 200 mgL^{-1} sulphate standard solution and settling three sampling cycles. Other parameters as described before.

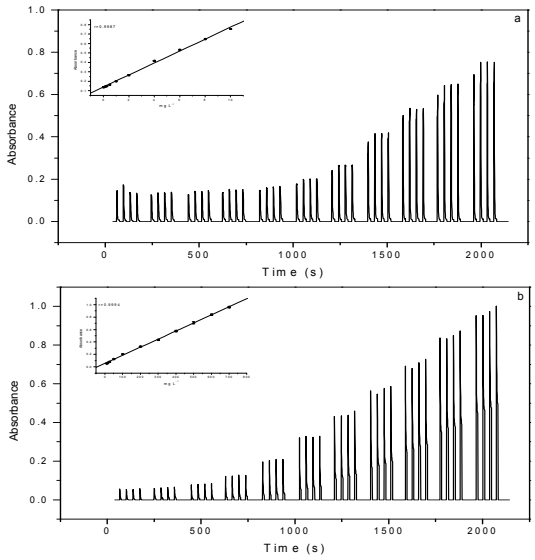

Figure 7. Records of the transient signals generated simultaneously. The set of record labeled as *a* correspond to chloride standard solutions of 0.0, 0.06, 0.125, 0.25, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0 mg L^{-1}, while the other one labelled as *b* is related with sulphate standard solutions of 10, 15, 25, 50, 100, 200, 300, 400, 500, 600, 700 mg L^{-1}.