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Robust flow–batch coulometric/biamperometric titration system: Determination of bromine index and bromine number of petrochemicals

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ABSTRACT

A flow–batch system was constructed and evaluated to perform coulometric titrations with biamperometric end point detection. The flow section of the system is employed for sampling by injecting a sample volume (50–300 μL) in a flow injection-like system. About 1.5 mL of a suitable carrier solution is delivered by a peristaltic pump in order to quantitatively transfer the sample to the system titration cell (2.0 mL total inner volume). The carrier contains the coulometric precursor for the titrant species. The cell contains two pairs of platinum electrodes used for coulometric generation of reagent and biamperometric detection and is actively stirred. The titrant species is generated and the titration is performed by the usual batch procedure with the excess of titrant being detected by biamperometry following the analysis of the titration curve. System operation is computer controlled and all operations are automated, including titration curve analysis and cell cleaning after the titration is ended. The system is characterized by its robustness because its operation does not depend on flow rates, and the work using coulometric methods which generate gases at the counter-electrode is not troublesome. The flow–batch system has been evaluated for determination of bromine index and bromine number (relative to the total reactive olefin content) in petrochemicals according to an ASTM procedure. Typical precision (R.S.D.) is between 0.5 and 6% for different petrochemicals whose bromine number/index vary from 1000 to 10 mg of bromine per 100 g of sample, respectively. Recoveries for standard additions are between 92 and 123% for 10 mg of Br_2 per 100 g increments and 98 to 101% for 100 mg per 100 g increments. Accuracy of the proposed system was evaluated against results obtained by the standard ASTM with no significant difference detected at 95% confidence level.

1. Introduction

The classical approach for a titration method is a batch procedure where a known quantity of sample is manually transferred to a titration cell. The titration itself is performed by adding known increments of titrant until all titrand species have reacted. The increments of titrant are obtained by volumetric, gravimetric or coulometric means.

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Coulometric generation of the titrant species precludes the use of standard solutions. Besides, it is also a very interesting form of providing reagents for systems based on true titration where the sample volume and the amount of reagent added up to the end point are the only parameters necessary for analyte quantification. This analytical method, although old, is still one of the most employed in product quality assay and in process control in countless industries. The Karl–Fischer titration for moisture determination, for instance, is performed at least 500,000 times a day around the world [1].

There are several papers in the literature dealing with the automation of the titration procedure [2–15]. Many of the recent ones present good reviews of the different approaches adopted with this objective and should be consulted for a more complete access to the variety of efforts approaching automation of the titration process [16,17].

Some approaches of automation have been suggested where the best characteristics of flow systems are combined with those of batch processing, aiming at the generation of more robust titration systems [12,13,16,17]. However, all the flow and flow–batch systems proposed so far present at least one drawback: either the system is strongly dependent on the flow rate used to delivery the sample and/or titrant or the system cannot deal with reactions which produce a gas inside the titration cell. Efforts have been carried out to avoid the generation of gas inside the titration cell of flow and flow–batch systems by physically separating the working electrode from the counter-electrode of a coulometric system [17,18]. However, it imposes a limit on the current that can be produced in a coulometric system due the increasing electrical resistance of the cell. This limit, in turn, restricts the dynamic concentration range of the titrator.

The determination of the bromine index (expressed as mg of Br_2 per 100 g of sample) and bromine number (expressed as g of Br_2 per 100 g of sample) in hydrocarbons is a common assay made in the petrochemical industries. It is a highly demanding determination usually made by means of a standard titration of the total olefins employing volumetry [19,20] or coulometry [21]. The method is based on the addition of bromine to the double bonds of the compounds present in the hydrocarbon fractions produced by the petrol refinery or the petrochemicals industries. Although the velocity which each olefin reacts with bromine (the titrant species) vary depending on position of the double bond in an aliphatic chain and on the overall hydrocarbon structure, the method is capable to producing the necessary information which may impact the chemical processes in the petrochemical and polymer industries.

The automation of classical methods, particularly with flow designs, can help industry laboratories improve their productivity and analytical performance, by minimization of the sample handling, increase of analytical frequency and substantial reduction of reagent consumption and analyses effluents.

The automation of the determination of bromine number has been described before using a flow system [18]. However, this system suffers from the drawbacks mentioned above, being dependent on flow rate, requiring at least one calibration step and not being able to deal with the presence of a gas phase during the titration process. This is especially true for systems employing spectrophotometric detectors to follow the titration progress.

In this work, a flow–batch system is proposed by combining the characteristics of a flow injection (FI) system with batch processing of the titration in a small cell where the coulometric generation of titrant and the monitoring of the titration curve can be achieved under robust conditions. This robustness is a consequence of its independence of flow rate, no need for standard solutions at all, and of the complete automation of the sampling operation and titration process. The proposed system was evaluated for the determination of bromine index and bromine number in a series of typical hydrocarbon fractions from the petrochemical industry. Its performance was evaluated by determining recovery in spiked samples and by comparison with the results obtained by the standard ASTM method.

2. Experimental

2.1. *Reagents, solutions and samples*

Analytical grade reagents and deionised water were always employed. The carrier/precursor solution employed in the proposed system was prepared mixing 73 mL of glacial acetic acid, 13.5 mL of dichloromethane and 13.5 mL of methanol. To this solution were added 10 mL of aqueous 2 mol L^{-1} KBr. This is the only solution necessary for the proposed system. Its composition was defined after preliminary evaluation of the amount of different hydrocarbon samples [from short (6 carbons) to long (12 carbons)] that could be readily dissolved in 1.5 mL. It was found that this solution can dissolve up to 300 μL of any of the hydrocarbon samples. This solution is stable for at least 2 months if stored in a closed flask at 10 °C.

The solutions employed for validation and recovery studies of the proposed system were prepared as described by the standard procedure [19].

Purified cyclohexene dissolved in appropriate volumes of toluene in order to produce solutions with bromine indices of 10, 100 and 1000 mg/100 g were used for precision. Accuracy tests were performed as recommended by the standard procedure [19] using the same solutions.

The olefin standards were prepared in toluene (Braskem product, 99.9%, w/w) from pure chemical reagents: 1-decene (Riedel, 96%, w/w), 1-heptene (Riedel, 95%, w/w), cyclopentene (Aldrich, 97%, w/w), cyclohexene (Merck, 99%, w/w), indene (Riedel, 95%, w/w), isoprene (Braskem product, 99.9%, w/w), 1,4-pentadiene (Dajac laboratories, >95%, w/w), cis-1,3-pentadiene (Fluka, >98%, w/w), styrene (EDN, 99.6%, w/w), alpha-methyl-styrene (Rhodia, >95%, w/w), 2-methyl-1-butene (Aldrich, 99%, w/w).

Samples of liquid hydrocarbons with average number of carbon from 6 to 12 were obtained from the petrochemical plant of the Braskem S.A., Camaçari, Brazil, and are representative of the classes of hydrocarbon produced by the company and of the bromine index and bromine number usually found during processing there. The set of samples consisted of hydrocarbon mixtures such as a naphtha, pyrolisis gasoline, xylenes, and pure products, e.g., toluene, *p*-xylene, benzene.

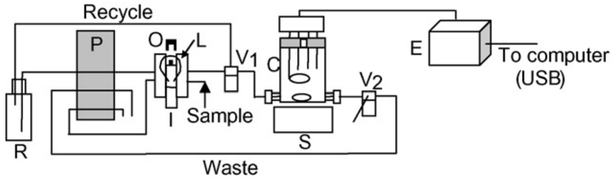

Fig. 1 – Schematic diagram of the flow–batch system. R, reagent reservoir; P, peristaltic pump; I, sampling injector; L, sample loop; O, opto-switch; V_1 and V_2, three-way solenoid valves; C, titration cell; S, magnetic stirrer; E, electronic circuits and computer interface.

2.2. *Flow–batch titration system*

Fig. 1 depicts a schematic diagram and an overview of the proposed automated titration system. A peristaltic pump (Ismatec IP8) supplied with Viton® tubing was employed to impel the solutions. The manifold was assembled using Teflon® tubing of 0.8 mm inner diameter. The system also has a proportional injection port arranged in a FI configuration, prepared to introduce a sample volume between 50 and 300 μL. The injector is made of Teflon® and is similar to a device described elsewhere [22]. A three-way mini solenoid valve (V_1) (National Research, NR-161T031) is placed between the injection port and the titration cell, permitting diversion of the flow back to the carrier solution reservoir, when required.

When valve V_1 is on, the flow is directed to a titration cell also made of Teflon®. The cell is placed on a motor-less magnetic stirrer. The cell's capacity is 2.0 mL. The lid of the cell contains two pairs of platinum electrodes made of platinum wires (0.5 mm diameter) covered with a Teflon® sleeve in order to expose only a part of the active surface to the inner solution. The lid also contains an open hole of 3 mm diameter. The coulometric pair of electrodes presents one electrode ending in a ring with 5 mm diameter while the counter-electrode has only 2 mm of the platinum wire exposed to the solution. Each one of the pair of electrodes employed for the biamperometric monitoring of the titration has 3 mm of the platinum wire exposed to the solution and this length is in the form of a small plate, obtained by hitting the wire with a hammer. These electrodes are ca. 1.5 mm apart.

On the electrodes the following reaction take place:

1. At the anode: $2Br^- = Br_2 + 2\ e^-$.
2. At the cathode (predominant reaction): $2H^+ + 2e^- = H_2$.

From the cell the manifold passes through another three-way solenoid valve (V_2) used, when on, to pump out the contents of the titration cell after the end of a determination.

2.3. *Electronic circuits and instruments*

The coulometric and biamperometric electronic circuits have been described elsewhere [17]. Analog switches controlled by the microcomputer connect the electrodes to the amperostatic or to the biamperometric circuits. The potential applied to the detection system was 200 mV. The different electrodes present in the cell are all independently connected or disconnected through the use of analog switches, controlled by the microcomputer running a user-tailored software. The generating electrodes are turned off before the detection system is turned on to monitor the titration.

Control of the system is made through a Data Translation Interface (DT9802) connected to a USB port of an IBM compatible microcomputer running a software written in VisualBasic.net. The interface presents 8 analog inputs to an analogue to digital converter (12 bits) and 12 programmable digital input/outut. The control of the peristaltic pump was made through a RS232 interface.

2.4. *System operation*

System operation is started by turning on the motor-less magnetic stirrer and pumping out any residual solution present in the cell. Then, the carrier solution is pumped for a pre-fixed time interval, long enough to ensure the manifold and titration cell have been filled with fresh carrier solution. Then the cell is drained again, the peristaltic pump is stopped, and the titration procedure is ready to start. Initially, a blank solution is first employed in place of the sample to determine the residual bromine index to be considered in the determination of this parameter for the real samples.

The sample is aspirated through the sample loop (whose volume has been previously determined) and the central part of the injection port is moved in order to introduce the sample loop into the carrier stream as the cell is being filled. The controlling software flags this operation by monitoring the logical state of the opto-switch Op1. Valve V_1 is turned on, diverting the carrier flow towards the titration cell. Enough time is used while pumping the solution to quantitatively transport the injected sample to the cell. The flow is stopped and V_1 is turned off. The coulometric titration is carried out under computer control and a complete titration curve is obtained and stored in the mass storing device of the computer. The titration is carried out by applying a pre-defined current for a defined time interval, until a given value of signal is observed by the biamperometric detection system. Finally, the titrated solution is removed from the cell by turning V_2 on and pumping the solution out to the waste reservoir. The same procedure is employed to titrate the blank in order to consider its contribution to the sample titration.

Once the program is completed, the cell is filled with the carrier solution, and the stirrer and peristaltic pump are turned off.

3. Results and discussion

This type of flow–batch system requires a few optimization steps to achieve good performance for determination of the bromine index and bromine number. The main concern is to set a system capable of dealing with samples in a wide range of olefin concentration. The best compromise was found by selecting the best sample volume, the coulometric current and the time this current is used to generate the titrant (Br_2). There are no optimization steps regarding flow rates and reagent concentrations because the standard titration procedure is,

Table 1 – Experimental conditions to perform the bromine index or bromine number of petrochemicals employing the proposed system

Bromine range (mg/100 g)	Coulometric current (mA)	Time interval (s)	Estimated titration time (min)
<50	1.0	2.0	2.5
50–200	5.0	1.0	3.5
200–500	5.0	2.0	5.0
>500	10.0	2.0	6.0

in fact, employed in the proposed system. The sample volume selected was (145.0 ± 0.3) μL, calibrated by delivering and weighting 10 injections of the sampling loop filled with distilled water.

The time for quantitative transport of this sample volume to the titration cell depends on the carrier flow rate and needs to be established previously. The carrier flow rate in the present system is 5.0 mL min^{-1}. Therefore, 18 s will delivery 1.5 mL of the carrier solution to the cell. This volume is enough to transport up to 300 μL of sample to the cell. The coulometric system can easily generate efficient currents of 1, 5 and 10 mA, as selected by the computer. This is facilitated by the fact that the system can operate with the cathode and anode directly immersed in the solution being titrated. The cell resistance drops substantially and inexpensive amperostatic circuits can be used. No side reaction is observed in the present case because the hydrogen generated at the cathode cannot react with the Br_2 produced by the anode. The system works well in the presence of the hydrogen bubbles generated inside the cell by the coulometric process because it escapes through a small diameter hole drilled in the cell lid. Residual bubbles inside the cell do not affect the electrochemical monitoring of the titration curve.

There are many possibilities in the way a titration can be conducted by using the proposed system. Successive small additions of the titrant are recommended to allow enough time between them while the hydrogen escapes to the atmosphere, before monitoring a stable biamperometric signal. The knowledge of the range of the bromine index or bromine number of a sample can help in optimizing the titration time. A series of procedures were defined for the concentration ranges found in routine analyses of the petrochemical industry. Table 1 shows the collection of procedures (currents and time intervals), suitable concentration ranges and typical titration times.

The protocol adopted for end point location searches for a pre-fixed current value from the biamperometric detector, which represent a fixed excess of bromine surpassing the end point of the titration. During the titration, the detector signal is monitored after each bromine addition until its current signal is greater than the pre-fixed value. Then the titration is stopped and the program automatically locates, by interpolation between the last two points, the exact time interval (translated into mass of bromine by Coulomb's law [21]) necessary to reach the pre-determined excess of bromine. In this way one does not need to be worried about reaching exactly that excess as it will be calculated from the titration curve data. Because the same procedure is adopted in the blank titration, the bromine in excess will be subtracted from the titration of the sample in order to achieve the real bromine amount necessary to react with the olefins. In addition, other protocols, such as extrapolations of linear segments of the titration curve observed before and after the end point, could be also employed for data treatment and end point location.

The system software accepts the density of the sample in order to perform the calculation of the bromine index or bromine number, which should be expressed in mass/mass units. A file containing the density values can be stored and

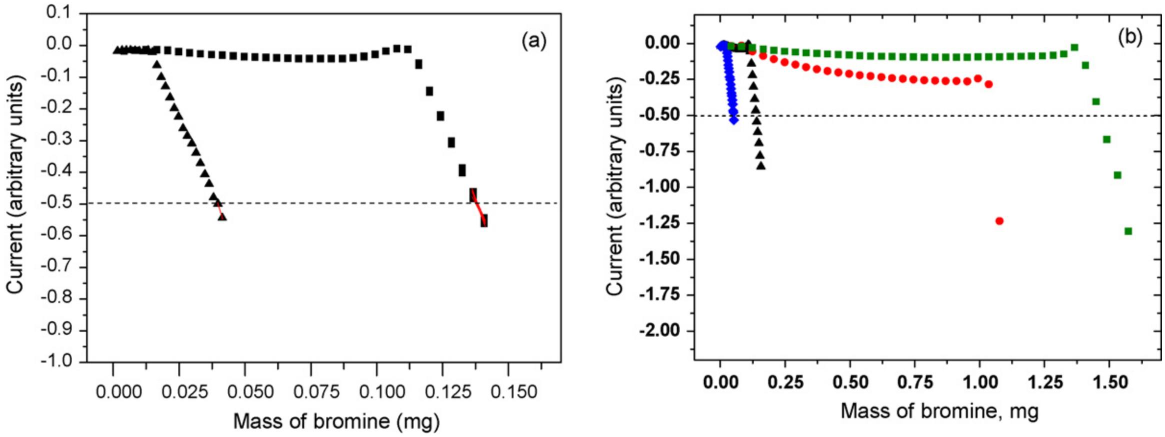

Fig. 2 – Titration curves obtained with the proposed system. (a) A blank test obtained by titrating the carrier and injecting toluene as sample (▲) and five replicates of a cyclohexene solution whose bromine index is 100 mg/100 g (■). (b) Titration curves obtained for the determination of two cyclohexene solutions with bromine index (▲) 100.1 and (●)1019.2 mg/100 g and two sample of petrochemicals presenting bromine number of (♦)12.8 and (■) 1754.6 g/100 g. Dashed lines indicate the signal threshold employed for determination of the titration end point.

Table 2 – Comparison of the results obtained for the bromine index of petrochemicals obtained by the proposed and reference method [18]

	Sample	Bromine index (mg/100 g)			
		Reference method [18]		Proposed method	
		Mean	R.S.D. (%)	Mean	R.S.D. (%)
1	Cyclohexene in toluene	9.8	4.7[a]	11.4	5.5[a]
2	Cyclohexene in toluene	100.2	0.3[a]	98.4	0.6[a]
3	Cyclohexene in toluene	987.2	0.7[a]	1011.9	0.3[a]
4	Sample I	11	–	12.0	0.7[b]
5	Sample II	95	–	112	4.7[b]
6	Sample III	885	–	1065	6.0[b]
7	Naphtha	95.0	–	96.7	–
8	Mixed xylenes	52.0	–	57.4	–
9	*p*-Xylene	<1	–	<1	–
10	Mixed xylenes	4.0	–	2.4	–

[a] R.S.D. (relative standard deviation) for 10 determinations. Synthetic samples of cyclohexene in toluene prepared as recommended for the standard procedure for accuracy evaluation.

[b] R.S.D. (relative standard deviation) for five determinations made by the proposed method. Only one determination was made for samples 4–10 using the standard method. Only one determination was made for samples 7–10 using the proposed method. Samples 4–10 are of real petrochemicals products.

retrieved by the user to facilitate the analysis of routine samples.

After the end point is found the following formula is employed for the index calculation:

$$\mathrm{BI} = \frac{\{m_{\mathrm{Br}_2}[\mathrm{sample}] - m_{\mathrm{Br}_2}[\mathrm{blank}]\}}{m[\mathrm{sample}](\mathrm{g})} \times 100 \qquad (1)$$

where BI is the bromine index. m_{Br_2}[sample] and m_{Br_2}[blank] are the bromine mass expressed in mg necessary to reach the end point for the titration of the sample and the blank, respectively. These are calculated from the coulometric current and total time interval necessary to reach the end point of the titration. The m[sample] is the mass of sample injected in the system expressed in grams. This is calculated by using the density of the sample and the pre-calibrated sample volume injected. The same formula applies to bromine number with the masses of bromine expressed in grams.

Fig. 2 shows some titration curves obtained with the proposed system. The format of the titration curves for the blank, standard and wide concentration of olefins from industrial petrochemical samples reflects the fact that bromine is consumed while the olefin is being titrated. When the stoichiometric point is reached the excess of bromine is detected by the biaperometric system and the current increases as excess bromine is generated inside the cell.

Table 2 shows a comparison between results obtained by proposed flow–batch titration system and the conventional volumetric procedure [19]. The repeatability of the system was verified by carrying out five titrations of a standard cyclohexene solutions, as shown in Table 2. For a petrochemical sample presenting an average BI of 12.0 mg/100 g, the standard deviation was 0.08 mg/100 g. This repeatability is suitable for routine analysis in the industry and compare well with that obtained by the standard volumetric method [19].

Recovery tests were made by adding known concentrations of cyclohexene to different samples of the industrial process. The mean recovery was determined as 98% with values in the range from 92 to 123%. Considering that this study employed additions as small as 20 mg/100 g in the BI, the results are quite acceptable for routine determinations. The accuracy was also evaluated comparing the results obtained for real and synthetic petrochemical samples obtained by the flow–batch system and the reference method. The results obtained for a wide range of concentration presented no statistically significant difference (95% confidence level) between the methods and are shown in Table 2.

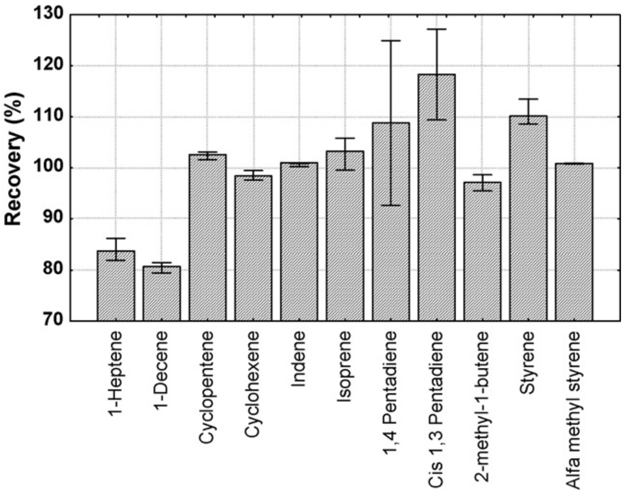

Fig. 3 – Recoveries for olefin standards in toluene using straight and branched chain olefins, cyclic olefins, conjugated and nonconjugated diolefins, and aromatic with unsaturated side chains. Each standard was analyzed by gas chromatography and the theoretical bromine index was calculated from such concentration and considering the expected result for each olefin according to table A1.1 of ASTM D1159. The range shown in each bar corresponds to the minimum and maximum observed recoveries from 5 replicates.

The detection limit, calculated as three times the standard deviation of a toluene sample, was 1.5 mg bromine per 100 g sample. The toluene sample has non-detectable olefin level, so it was used as a good blank estimate.

The proposed method has some drawbacks which are also observed in the conventional titration procedure. If the olefin to be titrated has a slow reaction with the titrant (bromine) under the titrations condition, negative errors are prone to occur, as it can be observed from the lower recoveries of straight-chain olefins in Fig. 3. On the other hand, it is important to mention the reactive olefins are the most important for the BI and NI parameter because they are responsible for most of the problems that the petrochemical industry faces when those parameters assume values higher than expected. From Fig. 3, it can be observed the system is accurate for quite different kinds of olefins, with recoveries ranging from 81 to 118%.

The reagent and sample consumption are reduced about 50 and 100 times, respectively, by employing the proposed system. This reflects in low waste generation by the laboratory and substantially reduces the cost of effluent treatments and laboratory environmental impact.

4. Conclusions

From both academic and industrial points of view this system represents an important achievement towards the automation of classical methods, bringing from the academy the advantages it has taken from flow systems. The flow–batch BI/BN titrator has addressed relevant scientific issues, overcoming some inconveniences that affected FI performance, namely flow rate dependence, detection interference from gas generation, handling of complex organic samples, titrant standardization, etc. The system contributed to improve the overall productivity and ecoefficiency of the laboratory by increasing the analytical frequency, drastically reducing wastes and minimizing analyst assistance.

The proposed system combines the best features of the flow–batch concept to produce a titration system that is characterized by its robustness. This is achieved mainly because the very low dependence of the system on flow rate stabilization and use of well established FI approach for the sampling step. Besides, the system does not require standards nor calibration while a true titration can be performed in according to standard procedures [19].

Even with the drastic reduction of sample and reagent consumption achieved, it has been demonstrated that the flow–batch system maintains the repeatability and accuracy necessary for routine purposes of the petrochemical industry.

The system also allows working with coulometric titrations that generate a gas at the counter-electrode. This is not possible when closed flow cells are employed and gets worse when spectrophotometric detection is chosen. Biamperometry is a suitable and inexpensive detection technique for bromine index and bromine number determinations and tolerates the presence of small gas bubbles during the titration. The range of concentration where the system can be used exceeds three orders of magnitude without any alteration in the manifold, and additional flexibility can be achieved by changing the sample loop, respecting the solubility limits of the sample volume in the carrier solution. Titration time is dependent on the values of bromine index and bromine number. Typical values are 3.5 and 6 min for $50 < \mathrm{BI} < 100$ and $500 > \mathrm{BI} > 1000$ mg/100 g, respectively.

The system can perform other types of determinations based on the same coulometric/biamperometric titration method described herein. It is presently being evaluated for moisture analysis in a membrane-free Karl–Fischer coulometric system.

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