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Infrared Turbidimetric Titration Method for Sulfate Ions in Brackish Water

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Abstract

In this work an infrared turbidimetric titration method is described for the determination of sulfate ions in brackish water. A suspension of barium sulfate is produced in an aqueous solution and/or brackish water sample by the addition of barium chloride solution and the turbidity is monitored with the help of an immersed infrared sensor. The developed sensor utilizes an optical system to measure the evolution of turbidity during the titration. This sensor is a simple device designed in the laboratory, consisting of two infrared diodes (LED), the first is an emitter and the second is used as detector (receiver). The data acquisition system is made with the help of a dataloger made on the basis of the microcontroller 16F877/874 accompanied with adaptable software both of them are self made. Concentration over 60 µg/mL of sulfate expressed as, SO_4^{2-} can be measured with high reproducibility, by this method without a preliminary treatment or dilution of the sample. The method determines SO_4^{2-} concentration of brackish water with RSD of < 1.2%.

Keywords: Sulfate ion; Infrared sensor; Turbidity; Titration; End-point.

Introduction

The determination of sulfate ions in water has an importance in connection with the quality of water resources, surfaces, brackish and sea water analysis [1]. Various methods exist for the sulfate ion quantification and some new spectrometric methods were reported during the last few years. Many of them require the simple precipitation method using barium chloride [2-5] or lead chloride [6,7]. All these methods use indigo light (450 nm) [3] or laser (680 nm) [2]. Batch spectrophotometer utilization cannot make a continued titration, but they refer to a calibration curve with great dependence by the experimental conditions. These systems are very difficult to insert in an on-line or flow-injection determination. In this work, IR-turbidimetric titration method is proposed. This titration method is very interesting and suited for the flow-injection determination of many other elements such as Cl^- and PO_4^{3-} ions. The used sensor can be easily used in on-line analysis according to the standard ISO7027 / EN 27027 for the surface water turbidity measurement. The standard ISO 7027 requires a measuring wavelength of 880 nm (near infrared light), a scattering angle 90°, and calibration of the instruments with formazine solutions. In our recently published work, we have successfully tested our infrared sensor for the determination of flocculated particles concentration in water treatment sludge [8,9]. In these works we have tested two simples data acquisition devises: The first consisting of a mulltimeter (MAS-View) with an RS232 connection and an electronic switcher and the second, is consisting of a numerical interface cart made on the basis of the microcontroller 16F84. A review of existing methods for the determination of sulfate ion yields several possibilities titration methods [10-12], but

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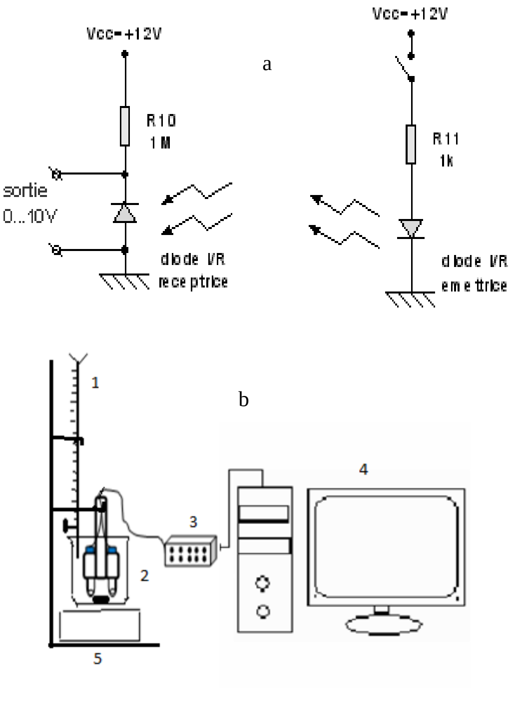
not IR-turbidimetric. The aim of this work, was to develop a simple, and a cost-effective immersed infrared sensor (emitting IR-LED at 940 nm, receiving IR-LED, scattering angle 0°-12°), which is able to quantify total suspended solid (turbidity) according to time and titrant volume in order to develop an accurate and fast procedure for the quantification of sulfate ion in brackish water. The analogical signal delivered by the IR-LED is communicated to PC via datalloger at exit RS 232 made on the basis of PIC 16F877/874. So data for change in turbidity versus volume of consumed titrant ($BaCl_2$) were transmitted to the PC via the datalogger accompanied with suitable data-acquisition software developed in LAAR laboratory (USTO) [13].

Materials and Methods

Infrared sensor

A simple device has been designed in the laboratory, consists of two infrared diodes (components commercially available and inexpensive), the first is an emitter and the second is used as detector (Fig. 1).



1: Burette with titrant $BaCl_2$; 2: Beaker and the infrared sensor; 3: datalloger; 4: PC; 5: Magnetic stirrer

Figure 1. **- a – Infrared sensor of turbidity electric schema; - b - Titrator assembly for infrared turbidimetric titration.**

The infrared LED are encapsulated in a small flask tube (0.5 cm diameter, 5 cm high); these tubes are disposed so that it can have a free rotation to regulate the incident angle and the sensor can easily be immersed in 250-mL beaker (Fig. 1a, 1b).

Datalogger system

The datalogger system (Fig. 2) consists of two parts: A small power supply (12Vdc) to feed the infrared emitter diode and the microcontroller based self rewired datalogger box. This system can be linked to a PC through the serial (RS232) port and piloted by software (Fig. 3). The datalogger box contains microcontroller PIC will 8 channels in-built 10 bit analog to digital converter PIC 16F877A.

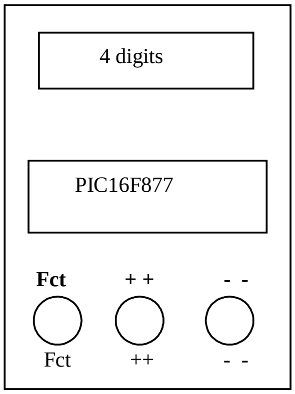


Figure 2. **Electronic datalogger and setting.**

At the start the datalogger (Fig. 2), goes to state 1= 00: 00 hour by default

State 1: Adjusting hours: increment (+ +) or decrement (- -)
Press the button (Fct) to go to state 2, otherwise, after 10s, the device switches to automatic acquisition.

State 2: Setting minutes: increment (+ +) or decrement (- -)
Press the button (Fct) to go to state 3, otherwise, after 10s, the device switches to automatic acquisition.

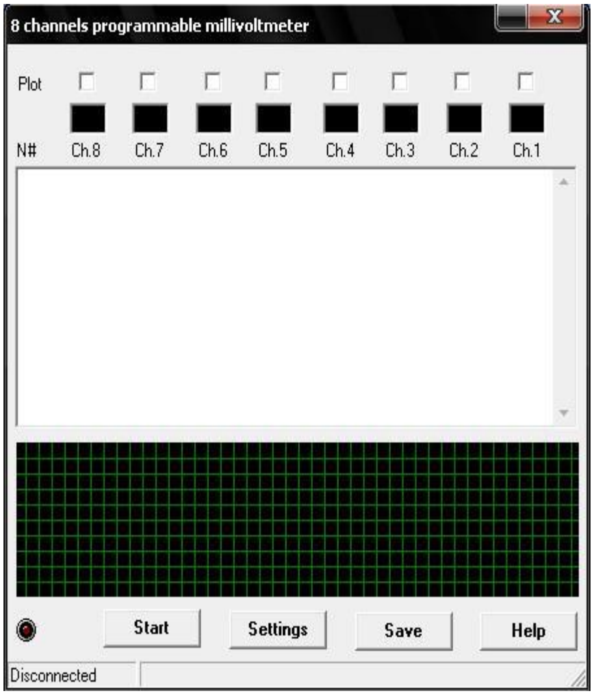
State 3 (*): Setting Cases 1 to 8: increment (+ +) or decrement (- -)
(see further explications on the table below)

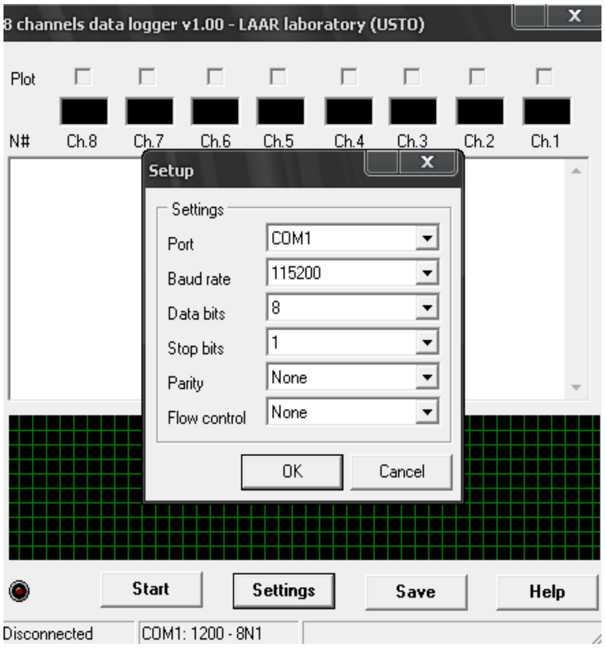
Press the button (Fct) to go to state 4, otherwise, after 10s, the device switches to automatic acquisition.
After 4 minutes (240s) the display is turned off to conserve battery life.

State 4: Setting display Channel A, B, C, D, E, F, G, H: increment (+ +) or decrement (- -)
(*) Details for the state 3:

CASE	Successive measured channels every second
Case1	A
Case2	A,B
Case3	A,B,C
Case4	A,B,C,D
Case5	A,B,C,D,E
Case6	A,B,C,D,E,F
Case7	A,B,C,D,E,F,G
Case8	A,B,C,D,E,F,G,H

The PIC16F877 microcontroller is equipped with an internal EEPROM of 256 bytes, can therefore store 256 coded 8-bit steps.





Port: COM1
Baud rate: 115200
Data bits: 8
Stop bits: 1
Parity: None
Flow control: None

Disconnected | COM1: 1200 - 8N1

Figure 3: **Acquisition Software and setting.**

Procedure for infrared turbidimetric titration

The turbidimetric titration method is a common method in many analytical laboratories and it is easily applied to the precipitation titration. In this work, infrared turbidimetric titration equation (1) of sulphate ion in 70 mL brackish water sample was monitored. Our attempt was to simplify the methodology using a simple data acquisition system without any change in the medium and or dilution of sample.

$$SO_4^{-2}\ (aq) + Ba^{2+}\ (aq) \longrightarrow BaSO_4\ (S)\downarrow \tag{1}$$

Some samples of brackish water from Bredeah desalination plant (Oran-Algeria) are used for the IR-turbidimetric titration. This plant 38,000-cubic-metre-a-day brackish underground water desalination, to supply drinking water for the residents of Oran, has been operational since 2004. The titration was set up as shown in (Fig. 1b):

The infrared sensor of turbidity was immersed after introducing the sample in the beaker. The sensor was submerged at the depth of 1.5 cm in the mixed solution. The titration was started under continuous stirring using a standard magnetic stirrer. A high and constant agitation degree was been maintained during the titration. Data for changes in turbidity as a function of consumed volume ($BaCl_2$) was transmitted to the PC by our acquisition system. Measurements obtained by the infrared sensor are expressed in millivolts, with acquisition frequency equal to one data per second.

Results and Discussion

The turbidity, which is in relation with total suspended solids, is deduced by measurement from the infrared quantity of light absorbed or reflected by the solid particles (attenuation of incident/scattering beam) contained in the water sample after chloride barium addition. So the used sensor, which is a low-cost titration detector was designed and fabricated on the known technique of attenuation. Infrared light (880-940 nm) was chosen because the interference of day-light is reduced. Our infrared sensor is a simple device, represents an immersed infrared sensor with light path length less than 3 cm. Instead of, a phototransistor relatively expensive we simply used an infrared LED for the signal reception and the product signal does not require amplification as the distance between the transmitter and receiver is small. So this immersed infrared sensor was expected to be as small as possible, but sufficiently robust. The angle at which the receiving LED is placed over the light source is correlated with the particles size in suspension. After several attempts a sensor that was designed easily adjustable and fitted perfectly to different types of suspension. After several tests it was found that $BaSO_4$ suspension measurement must be performed at O ° (attenuation), because in this case, the results are significant. However, the geometry of the sensor can results in the collection of light scattered trought range 0 ± 180. But, it should also be noted that determination of the ideal angle for any suspension is not easy and depends on several parameters (medium, intensity of incident beam, the distance between IR-LED, temperature). Since, suspended material in the sample can interfere with the analysis, it is necessary to filter suspended matter from solution prior determination. Any coloured substance that absorbs radiation at the wavelength which is chosen for the analysis can also interfere. The size of the suspended barium sulphate particles has an effect upon the amount of radiation which is scattered during the turbidimetric measurement. Consequently, it is necessary to carefully control those experimental parameters, such as rate of mixing and reaction time, which can affect particle size.

The generated signal after its transformation signal with the help of the datalloger, the software ensures the transfer of the experimental data to PC. The export of the data to Excel or Origin and there treatment give the awaited curves and results. To determine the concentration of sulfate ion a solution of sodium sulphate (reference sample) and samples of brackish water, after adding the first drop of barium chloride, the titrate became turbid and, as the titration continued, the transmitted light detected gradually decreased. The resulting titration curves (Fig. 4) were evaluated graphically.

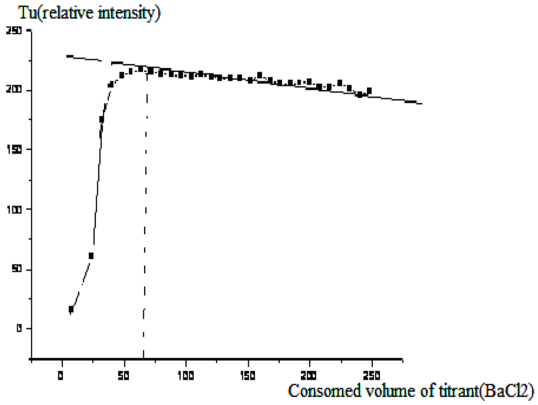


Figure 4. **IR-turbidimetric titration curves of sufate ion in brackish water. [barium chloride $BaCl_2$(C = 0.0123 mol. L^{-1}).**

The end point determination for the IR-turbidimetric titration is easy and accurate. The results confirm that IR-turbidimetric titration is feasible and gives very reliable results. The sulfate contents of various brackish water samples were determined in this method and compared with values obtained by the standard procedure using a spectrometer (650 nm) and glycol-ethanol as a medium. And using the linear calibration curve (C= 121.7A; R^2= 0.979) in the spectrophotometric method obtained with the sulphate standards solutions of $(NH_4)_2SO_4$. The results obtained are given in Table 1; the titration was repeated six times.

Table 1. **End-point Indication by IR-turbidimetric and spectrometric titration for brackish water sample**

N° Essays of Brackish Water sample	*End point of IR-tubidimetric titration V(mL) - C(ppm)*	*End point of spectrometric method Abs .- C(ppm)*
1	71.20 - 1220.50	0.850 - 1203.9*
2	71.5 - 1206.10	0.880 - 1241.1
3	73.5 - 1239.84	0.860 - 1218.3
4	71.5 - 1206.10	0.880 - 1241.1
5	71.4 – 1204.41	0.850 - 1203.9
6	72.5 – 1229.71	0.870 - 1236

* The sample was 03 times diluted for spectrometric determination

The concentration of sulphate in each sample of brackish water was estimated. The results are given together with those obtained by proposed method with the spectrometric method, it can be seen that the results of at least the same precision. A statistical evaluation of the results shows that the relative standard deviation is RSD = 1.2 % for n=6.

Conclusion

Our experiments show that with a simple infrared sensor and a simple titrator assembly, sulfate ion in brackish water can be quantified by infrared turbidmetric titration. In this simple method, exploitable curves can be obtained and the great advantage is its instrumentation (experimental data acquisition) which makes it accurate, rapid and useful for on line and flow-injection measurement. This method is economic and ecologic as the addition of conditioning reagent is avoided. Consequently, the methodology is very simple and represents a better alternative for the sulfate determination in dilute solutions and surface water.

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