ORIGINAL ARTICLE

Combination of FIA-CL Technique with ion-exchanger for determination of sulphate in various water resources in Erbil City

Diyar Salahuddin Ali *, Azad T. Faizullah

Department of Chemistry, University of Salahaddin, Erbil, Iraq

Abstract   A new flow injection chemiluminescence system is developed for determination of anions like sulphate. The method is based on the displacement of an equivalent amount of bromide ion on a Br^- from an ion-exchange minicolumn by sulphate. The released Br^- then reacts with BrO_3^- in acidic medium to produce bromine water which catalyzes the Luminol/H_2O_2 chemiluminescence. Working conditions for these determinations were optimized. The emission intensities produced were recorded as peak height (mm) on a chart recorder and they were proportional to the amount of sulphate injected. This method allowed determination of 0.96 mg/l SO_4^{2-}.

   The developed FIA-CL system was applied for determination of sulphate in water (well and waste water) in different regions in Erbil City – North of Iraq. Interference effects of various anions were eliminated by inserting a suppressor minicolumn in the FIA-CL system after injection port, which allowed for sulphate only to pass through. The method provided a very simple, rapid and sensitive method for sulphate determination without any pretreatment. The present method was applied for sulphate and could be used for other ions with some improvement in the suppressor column.

* Corresponding author.
  E-mail addresses: dr.diar@uni-sci.org, diyar@kurdchemists.org
(D.S. Ali).

1. Introduction

Sulphate is a highly widespread anion, and its determination in environmental objects (such as sweet, mineral and sea water; atmospheric precipitation, in particular, acid rain), in various products and raw materials of chemical and pharmaceutical industry, in food, etc., has been an important task. Existing methods for sulphate determination have several drawbacks such as long duration and unacceptability for low concentrations (gravimetric methods); laboriousness, insufficient selectivity and reproducibility (optic methods including nephelometry and turbidimetry) (Lomako et al., 2006).

Different methods used for determination of sulphate were done. A novel capillary electrophoresis (CE: one of chromatographic methods) with chemiluminescence (CL) detection method for determination of sulphate has been developed. This method is based on the chemiluminescence reaction of potassium ferricyanide with luminol in sodium hydroxide medium sensitized by sulphate (Shuting et al., 2009).

The diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR for knowing the functional groups and determined directly) is used as a sensitive tool for sulphate determination in water and environmental samples (Santosh et al., 2007).

Also sensitive SIA method was developed for sulphate determination in real samples such as fuel and water (Fabio et al., 2006).

The present work is described for the determination of sulphate in water. The method is based on the generation of bromine water from the $BrO_3^- - Br^- - H_3O^+$ reaction; the bromine then reacts with H_2O_2 to liberate oxygen, which will oxidize luminal in an alkaline medium. The sample sulphate displaces an equivalent amount of Br^- from an exchange column. The Br^- then reacts with BrO_3^- in an acidic medium to produce bromine water which catalyses the luminal/H_2O_2 CL system as mentioned before.

For the determination of sulphate in water a new method is described. It is based on inserting a combined suppressor column into the FIA-CL manifold for providing the selectivity of anion determinations. This new method can apply for the determination of sulphate in different well waters in Erbil City.

A sample size of (60 μl) was used with a flow rate (3.7 ml/min). The range of determination were 48–960 mg/l; also 0.96 mg/l considered as a detection limit for sulphate determination using a combined suppressor column. Linear regression of the Log–Log plot of concentration (mg/l) versus chemiluminescence intensity (peak height (mm)) gave a correlation coefficient of 0.999 for sulphate in the concentration range studied.

The rapid growth of flow injection analysis which utilizes chemiluminescence technique reflects its many advantages relative to conventional procedures. The chemiluminescence from the oxidation of luminal by hydrogen peroxide in alkaline medium has been used to detect and determine the trace amount of material in a variety of analytical techniques (Ali and Faizullah, 1999).

Ion-exchange can be incorporated in the flow injection manifold by using a resin column in the sample stream and as a result a simple and stable system is obtained (Bergamin et al., 1980).

Compared with other analytical methods (e.g. spectrophotometrically, gas chromatography and mass spectrometry) (Yang et al., 1997), chemiluminescence is highly sensitive, selective and accurate for sulphate determination.

The fundamentals of suppressor columns used for improving the selectivity of anion determination have been described extensively (Faizullah and Townshend, 1986). They can involve one of a number of types of reactions. One is the conversion of an ionic species to a molecular form, e.g., hydroxide to water or hydrocarbonate to carbon dioxide and water.

2. Experimental

2.1. Apparatus

A multi channel peristaltic pump (Desaga), a six way injection valve with a 60 μl sample loop, silicon rubber tubing (0.5 mm i.d.), a reaction cell (60 μl). A photo tube of a spectrophotometer (Type Ultra spec. LKB 4050 UV/Visible) as a detector x-t recorder (Type PM 8251 A Philips). Power supply and micro voltmeter were used as associated electronics.

2.2. Reagents

Sodium carbonate solution; (0.1 M), dissolve 10.599 g of Na_2CO_3 in 1 l of water.
Hydrogen peroxide solution; (0.1 M), dilute 8.596 ml of 35% H_2O_2 to 1 l of water.
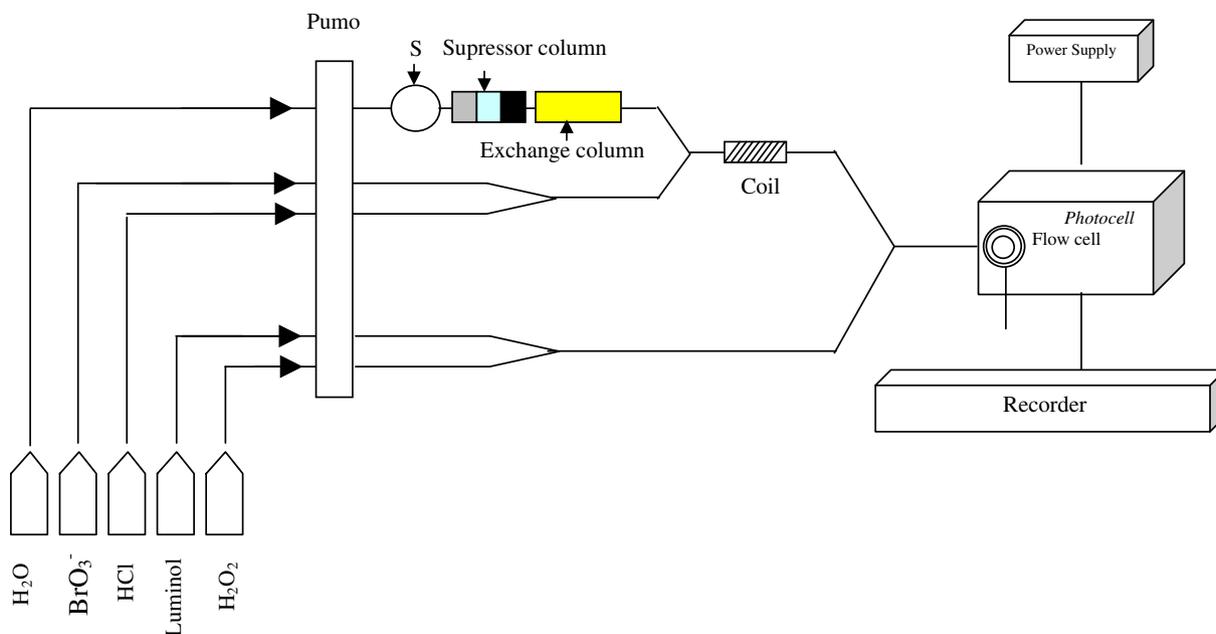
Figure 1 Combined suppressor column with FIA-CL system used for sulphate determination.

Luminol solution; (1×10^{-3} M), dissolve 0.17717 g of luminal in 1 l of 0.1 M Na_2CO_3 solution.

Potassium bromate solution; (0.4 M), dissolve 33.402 g of $KBrO_3$ in 500 ml of water.

Potassium bromide solution; (0.1 M), dissolve 5.95 g of KBr in 500 ml of water.

Hydrobromic acid solution; (1 M), dilute 11.2 ml of concentrated HBr to 500 l of water.

Hydrochloric acid solution; (0.5 M), dilute 20.7 ml of concentrated HCl to 500 l of water.

Ammonium sulphate solution; (1×10^{-2} M), dissolve 0.13214 g of $(NH_4)_2SO_4$ in 100 ml of water.

2.3. General procedure

Fig. 1 shows a schematic diagram of the FIA-CL system used in which sulphate 60 μl is injected through the sample loop into a stream of distilled water and the signal is recorded as a single symmetrical peak.

Streams of HCl and $KBrO_3$ are mixed and then combined with a carrier stream of the sample, the resultant stream was then mixed in a flow cell with another combined luminol/H_2O_2 stream. During this stage no emission signal occurs due to the absence of Br^-, which is essential to form bromine water, but when sample is injected they pass through a suppressor column Fig. 2, which includes a cation exchanger resin (H^+-form) which is used to remove cations, whereas the second cation exchanger (Ag^+-form) is used to remove anions, but some of the silver ions could be passed through in this column due to solubility factor, hence an anion-exchanger resin (Cl^--form) is used to trap any silver ion eluted and only the sulphate passes through in this column. Then they displace an equivalent amount of Br^- on the exchanger column. The latter reacts with BrO_3^- in acidic medium to produce bromine water which catalyses the luminol/H_2O_2 CL system.

3. Results and discussion

3.1. Optimization

The flow injection chemiluminescence system shown in Fig. 1 was used to determine sulphate in water samples according to two main stages

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \tag{1}$$
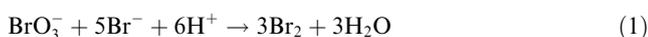
This stage led to a stable base line of the reaction on a chart recorder.

First stage before sample injection: Streams of $KBrO_3$ and HCl are mixed and then combined with a carrier stream of the sample. The resultant stream is mixed in a flow cell with another combined luminol/H_2O_2 stream. During this stage no emission signal occurs due to the absence of Br^-, which is essential to form bromine water as shown in the Eq. (1)?

Second stage after sample injection: Injection of 60 μl of sulphate sample displaces an equivalent amount of Br^- on the exchanger column. The latter reacts with BrO_3^- in an acidic medium according to Eq. (1) to produce bromine water which catalyses the luminol/H_2O_2 chemiluminescence system. The emission intensities produced were recorded as peak height (mm) on a chart recorder and was proportional to the amount of sulphate concentration injected.

Bromine is reacted with H_2O_2 to liberate oxygen, which is necessary for oxidizing luminal in alkaline medium. Generation of bromine water from ($BrO_3^- - Br^- - H_3O^+$) system occurs according to Eq. (1), which in turn reacts with hydrogen peroxide as followings.

$$H_2O_2 + Br_2 \rightarrow O_2 + 2H^+ + 2B_r^- \tag{2}$$
$$2H^+ + 2Br^- + H_2O_2 \rightarrow Br_2 + 2H_2O \tag{3}$$
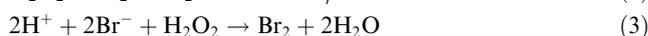
The final result for Eqs. (2) and (3).

$$2H_2O_2 \rightarrow 2H_2O + O_2$$
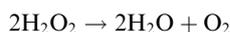
For removal of all interferences in the determination of sulphate in real samples (water), we used a combined suppressor column. This column removed all anions and cations except sulphate; in this case only sulphate can be determined as shown in Fig. 1.

3.2. Reactant concentration

Effects of various reactant concentrations as shown in Fig. 1 were optimized.

3.2.1. Bromate concentration

Solutions containing (1×10^{-3} M) H_2O_2, (1×10^{-4} M) luminol, (0.1 M) HCl and different bromate concentrations (0.01–0.4 M) were prepared in 50-ml calibrated flasks. Column of 3 cm length was used in this work. Distilled water produced no significant response. Fig. 3 shows the variation of CL-intensity, expressed as peak height in (mm) ($n = 3$). A $KBrO_3$ concentration of (0.17 M) was chosen for optimum sensitivity and reproducibility for the determination of sulphate when using a combined suppressor column. Higher concentrations were not studied owing to the low solubility of $KBrO_3$.
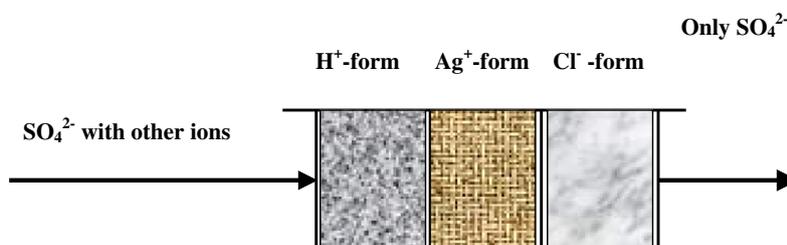
Figure 2 Arrangement of suppressor column used for eliminating interfering effects in sulphate determination.
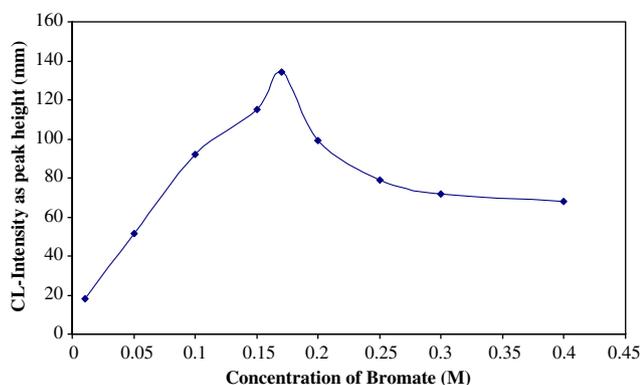
Figure 3 Effect of BrO_3^- concentration on CL-intensity for sulphate determination.
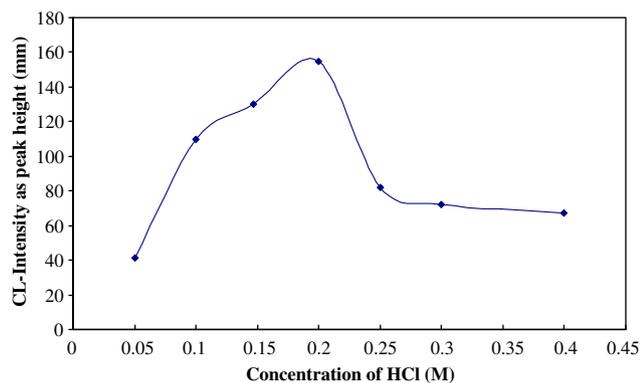
Figure 4 Effect of HCl concentration on CL-intensity for sulphate determination.

3.2.2. HCl Concentration

Using 0.17 M $KBrO_3$ (see above) and keeping the luminol and hydrogen peroxide concentrations at 1×10^{-4} and 1×10^{-3} M, respectively.

Solutions containing different acid concentrations (0.05–0.45 M) were prepared in 50-ml calibrated flasks. Fig. 4 shows the variation of chemiluminescence intensity, expressed as peak height in (mm) ($n = 3$).
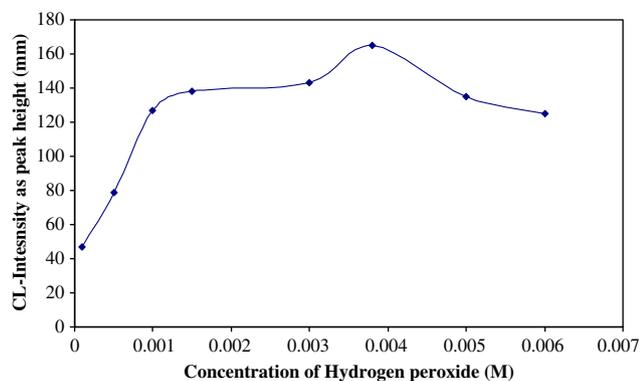
Figure 5 Effect of H_2O_2 concentration on CL-intensity for sulphate determination.

It can be seen that 0.147 M gives the largest emission signal for sulphate by using a combined suppressor column.

3.2.3. Hydrogen peroxide concentration

Using 0.17 M $KBrO_3$, 0.147 M HCl and 1×10^{-4} M luminol concentration for sulphate determination, solutions containing different concentrations (5×10^{-5}–1×10^{-2} M) were prepared in 50-ml calibrated flasks. Fig. 5 shows the result obtained when using a combined suppressor column for the determination of sulphate in water. A 3.86×10^{-3} gave the largest emission signal.

3.2.4. Luminol concentration

Under the optimized concentrations of H_2O_2, $KBrO_3$, HCl and other physical parameters the effect of solutions containing different luminol concentrations (5×10^{-6}–1×10^{-3} M) prepared in 50-ml calibrated flasks, using 0.1 M Na_2CO_3 solution to complete the prepared solutions. Fig. 6 shows the variation of chemiluminescence intensity expressed as peak height in (mm) ($n = 3$). The concentration 1×10^{-4} M luminol was select as optimum for sulphate determination.

From these experiments the optimum reactant concentrations were found to be 0.17 M $KBrO_3$, 0.147 M HCl, 3.86×10^{-3} M and 1×10^{-4} M luminol for determination of sulphate in water by using a combined suppressor column.
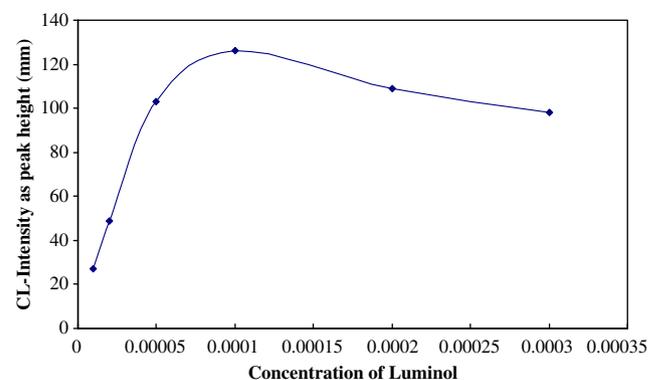
Figure 6 Effect of luminol concentration on CL-intensity for sulphate determination.

Table 1 The statistical treatment of calibration results of sulphate.

Linear range mg/l	Slope (b)	Intercept (a)	r
9.5–48	0.541	45.6	0.999

Table 2 Precision of the response for determination of sulphate via CL-intensity measurements: ($n = 5$).

Sample concentration (mg/l)	Mean of peak height (mm)	RSD (%)
960	137.98	0.06
480	122.03	0.077
96	100.06	0.057
48	66.98	0.08

3.3. Length of exchanger column, combined suppressor column and delay reaction coil

Effects of different column lengths (2–4 cm) on the CL-intensity were studied. Emission signal recorded as peak height (mm) was 3 for sulphate determination, where the best combined suppressor column lengths were found to be H^+-form (0.5 cm), Cl^--form (1.5 cm) and Ag^+-form (2 cm) lengths for sulphate determination.

Delay reaction coil length Fig. 1 of 40 cm gave the best result for sulphate determination.

3.4. Calibration graph

The flow injection chemiluminescence system shown in Fig. 1 was used for the determination of sulphate. Calibration graph for sulphate was plotted between sulphate concentration and chemiluminescence intensity. The statistical treatments according to the linear equation are mentioned in Table 1.

The linear relationship between the dependent value of (Y) and analyte concentration (x) according to linear equation.

It was found that the calibration graph is linear in the concentration range of 9.5–48 mg/l sulphate.

The precision of the signal was studied by injection of 60 μl of different concentrations five times in a respective manner. Tables 2 and 3 indicate the statistical treatments.

According to the optimum conditions detection limits of 0.96 mg/l sulphate were obtained. The signal to noise was found to be 3.

3.5. Application

3.5.1. Determination of sulphate in water

In the determination of sulphate in real sample (water), two important considerations must be taken into account. First, removing interferences for some essential anions associated along with sulphate such as nitrate, chloride, and carbonate. Second, comparing results of this procedure with a standard method for the determination of sulphate.

Table 3 Determination of sulphate in well water samples for North of Erbil.

No.	Region	Temp. (°C)	Depth (m)	Data obtained by the proposed method (mg/l)	SD $n = 5$	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	Kuran Ainkawa	21.5	154	112	0.056	110	1.81
2	Sixty Street	21	73	258	0.050	252	2.38
3	Rizgary	21.5	116	107	0.071	109	−1.83
4	Building Project	21	146	102	0.047	106	−3.77

Table 4 Determination of sulphate in well water samples for South of Erbil.

No.	Region	Temp. (°C))	Depth (m)	Data obtained by the proposed method (mg/l)	SD $n = 5$	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	Manticawa	21.5	137	219	0.071	221	−0.90
2	Azady	21	138	187	0.079	182	2.74
3	Roonaky	21.5	125	121	0.058	123	−1.62
4	Al-Adl	21	131	132	0.041	140	−5.7

Table 5 Determination of sulphate in well water samples for West of Erbil.

No.	Region	Temp. (°C)	Depth (m)	Data obtained by the proposed method (mg/l)	SD $n = 5$	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	Nawroz/2	21.5	161	182	0.041	187	2.67
2	Nawroz/4	21.5	151	168	0.039	165	−1.81
3	Kurdistan	21.5	136	201	0.067	199	−1.00
4	Al-Umal	21	160	287	0.055	289	0.69

Table 6 Determination of sulphate in well water samples for East of Erbil.

No.	Region	Temp. (°C)	Depth (m)	Data obtained by the proposed method (mg/l)	SD $n = 5$	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	Shorsh	21.5	203	99	0.089	98	−1.02
2	Braiaty	21.5	156	208	0.078	210	0.95
3	Raparin	21.5	168	153	0.054	156	1.92
4	Officers	21	170	145	0.065	148	2.02

Table 7 Determination of sulphate in well water samples for Center of Erbil.

No.	Region	Temp. (°C)	Depth (m)	Data obtained by the proposed method (mg/l)	SD n = 5	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	Khanaqah	21	186	201	0.074	199.7	−0.65
2	Ashty/9	21.5	148	105	0.052	104.3	−0.67
3	Al-Arab/1	21	39	376	0.065	380	1.05
4	Shaikh Choly	21	–	450	0.055	449.2	−0.17

Table 8 Determination of sulphate in well water samples for Industrial Region.

No.	Region	Temp. (°C)	Depth (m)	Data obtained by the proposed method (mg/l)	SD n = 5	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	North Industrial/2	21.5	138	167	0.050	166.5	−0.30
2	North Industrial/1	21.5	106	287	0.048	288	−0.34
3	North Industrial/3	21.5	–	165	0.032	168	1.78
4	Center Storge's	21	149	398	0.087	401.2	0.79
5	Al-Mamel/1	21.5	140	209	0.074	208.5	−0.23
6	Al-Mamel/4	21.5	150	123	0.062	123.22	0.17

Table 9 Determination of sulphate in wastewater samples.

No.	Region	Data obtained by the proposed method (mg/l)	SD n = 5	Data obtained by the EDTA method (mg/l)	Relative error (%)
1	Mantikawa	217	0.052	217.4	0.18
2	Raparin	102	0.042	102.5	0.048
3	Rizgary	220	0.065	219	−0.45
4	Narowz	503	0.087	504.5	0.29
5	Khanaqa	290	0.048	291.2	0.41
6	North Industrial	102	0.056	102.5	0.48
7	South Industrial	114	0.066	115.2	1.041
8	Hospital	112	0.049	114.3	2.01

To achieve that, it was necessary to make an instrumental modification by inserting a mini-combined suppressor column (H^+-form, Ag^+-form, Cl^--form) into the FIA-CL system shown in Fig. 1 after the sample injection port. The function of the column is illustrated in Fig. 2.

This study includes the determination of sulphate in drinking well waters regularly, and the City was divided geographically into five areas {North, South, Center, East and West of Erbil} to determine the water quality with respect to the presence of sulphate in the water; while many random samples were taken from wastewater in Erbil City to determine sulphate in these samples.

3.5.2. Sampling

Water samples were taken from 20 locations including 26 wells and 8 locations for wastewater, and the sulphate was determined in these samples with respect to temperature and depth in meters.

3.6. Results and discussion

Sulphate was determined according to optimum conditions for the FIA-CL manifold which include suppressor column as shown. The results obtained were compared with the standard procedures of tables including World Health Organization (WHO) classification 1984.

The results are shown in Tables 4–9.

7. Conclusion

This developed method is used to analyze the sulphate in well waters, natural waters and wastewater. The concentration of SO_4^{2-} measured by this method ranged between 2.33 and higher than 298 mg/l. We obtained the same results by EDTA Titration method. This procedure should not be used for highly contaminated wastewater samples with a high solid

content. An alternate procedure will be needed for clean type of samples. The method does not require uncommon or expensive reagents. The proposed procedure provides a very simple, rapid and sensitive method for sulphate determinations. However, it is essential to improve its selectivity so that one or two anions can be determined in the presence of the other. This work is used to determine the concentration of sulphate in water.

References

Ali, Diyar S., Faizullah, Azad T., 1999. JDU 2, 2 (special issue).

Bergamin, F.H., Jacintho, B.F., Zagatto, A.G., 1980. Analytical Chimica Acta 117, 81.

Fabio, S., de Oliveira, Mauro, K., 2006. Talanta 68, 992.

Faizullah, A.T., Townshend, A., 1986. Analytica Chimica Acta 179, 233.

Lomako, S., Astapovich, R.I., Nozdrin, O.V., 2006. Analytica Chimica Acta 562, 216.

Santosh, K., Verma, M., Kanti, D., 2007. Talanta 71, 1546.

Shuting, L., Janshi, W., Shulin, Z., 2009. Journal of Chromatography B 877, 155.

Yang, F., Troncy, E., Vinay, P., 1997. Clinical Chemistry 43, 657.