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Original article

Trace identification of sulfate anion in bottled and metropolitan water samples collected from various provinces of Saudi Arabia

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ABSTRACT

Water quality especially drinking water is highly significant to human lives. To access the safe and secure drinking water, nowadays it has become an issue of global concerns. A novel method using an ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) was proposed to analyze sulfate level in bottled and metropolitan water collected from various provinces of Saudi Arabia. The chromatographic analysis was achieved within 1 min with reversed phase Waters Acquity® BEH C_{18} column and a triple quadrupole mass spectrometer. The performance of the optimized system was established, attaining linearity (r^2 > 0.999) over a wide-ranging concentration from several below hundred mg/L to the detection limit of sulfate. In terms of relative standard deviation of the samples (RSD%), the excellent run-to-run (<2%, n = 5) and day-to-day (<4%, n = 5) precisions were achieved when examining a sulfate standard (0.01 mg/L) and non-spiked bottled water sample with the concentration of sulfate (4.76 mg/L). The developed method is helpful to identify sulfate in bottled and metropolitan water samples. Sulfate content in the bottled water ranged between 3.31 and 76.22 mg/L, while higher level was determined (36.78 to 268.42 mg/L) in metropolitan water samples. The excellent quality parameters and insignificant matrix effects achieved during analysis have made favorable to analyze sulfate in water samples, and offered advantages over conventional techniques and rigorous sample preparation procedures.

1. Introduction

Water quality especially drinking water is highly significant to human lives. To access the safe and secure drinking water, nowadays it has become an issue of global anxieties. More than one billion people failed to access safe drinking water from developing countries (WHO, 2008; Frengstad et al., 2010; Alizadeh and Mahjoub, 2015). The excessive richness of nutrients level in the aquatic environment can be unsafe to human beings and can cause water eutrophication. Sulfate is known to be a major anion in aquatic environment, and can be present naturally or result of various point sources includes municipal sewage treatment plants, industrial discharges for instance plating industries, textile mills, tanneries, mining and pulp mills, and use of coal and petroleum products (Greenwood and Earnshaw, 1984; Moore, 2012; de Karla et al., 2018). Overspill from manure farming lands also adds sulfate to water reservoirs (Powell and Martens, 2005). In 1977, the US National Academy of Sciences has illustrated taste levels in drinking water ranged between 250 and 1000 mg/L for calcium sulfate, 250 to 500 mg/L for sodium sulfate and 400 to 600 mg/L for magnesium sulfate (National Research Council, 1977). Nevertheless, enhancing sulfate concentration in surface water offers a critical sign for water acidification in reservoirs that effect on quality of water and health concern (Shakirullah et al., 2005; Stambuk-Giljanovic, 2005; Luke et al., 2014).

Several analyses were carried out to identify the toxicity of sulfate in human beings (Cicchella et al., 2010). Cases report that the consumption of sulfate has shown catharsis especially in adult population (Morris and Levy, 1983). Cathartic effects are frequently

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observed by the individuals drink water containing sulfate in levels higher than 600 mg/L (USPHS, 1962). In addition, the high consumption of sulfate has also caused the dehydration in humans (Backer, 2000; Backer et al., 2001; Fingl, 1980). Many authors have also reported the gastrointestinal disease like diarrhea especially infants when they are exposed to drinking water having sulfate at amounts between 630 mg/L and 1150 mg/L (Chien et al., 1968). Owing to sulfate availability in water and its health benefits, it is require to formulate a sensitive, rapid, and selective technique for the identification of such kind of possibly toxic pollutants in drinking water.

Numerous analytical methods for instance flow-injection analysis (Fung et al., 2008), high performance liquid chromatography using ion-pair method (Zuo and Chen, 2003), laser Raman spectroscopy (Murata et al., 1997), spectrophotometer(de Oliveira and Korn, 2006), sequential injection analysis (van Staden and Taljaard, 1996), turbidimetry (Kolmert et al., 2000), sequential injection analysis-multivariate curve resolution(del Río et al., 2010), capillary electrophoresis (Kulka et al., 2006), ion exchange chromatography (Barry et al., 1978; Biesaga et al., 2004) and gravimetric method (Kolthoff et al., 1969) have been reported for sulfate determination from water samples. The drawbacks of these described traditional analytical methods are time consuming, low sensitive and selective, and require sample pre-treatment, high amount of samples and solvents. To overcome such limitations, the introduction of a fast analysis of sulfate is of great attention. Recently, we have also developed fast, sensitive and selective methods based on UPLC–MS/MS for the determination of inorganic compounds in drinking water and non-alcoholic beer samples. For example, UPLC–MS/MS based analysis was used for the determination of bromate in drinking water (Alsohaimi et al., 2012), UPLC-electrospray mass spectrometry (ESI/MS) method for bromate analysis in non-alcoholic beer (Khan et al., 2014). UPLC–ESI/MS method was proposed for the determination of nitrate, bromate and nitrite in drinking water (Khan et al., 2013; Khan et al., 2016). These optimized methods have been found very rapid, sensitive and selective during the analysis of inorganic compounds in such type of samples.

The main aim of present study was to develop quantitative and qualitative analytical method for the determination of sulfate in drinking water taking benefits of the reduction of analysis time and solvent consumption, and increase in selectivity and sensitivity. Taking these advantages into consideration, we therefore developed an analytical tool based on UPLC–MS/MS for the analysis of sulfate in drinking water. The outcomes of the present findings obtained with this novel method and outcomes achieved on various water samples approve that they are enough to offer it as a new standard method for the rapid and reliable analysis of sulfate in drinking water.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and solvents applied in the present study were of analytical grade (AR) or HPLC grade, purchased from Merck (Darmstadt, Germany). Sodium sulfate (purity ≥ 99%) was supplied from Merck (Munich, Germany). For sample preparation, Milli–Q water was used which was obtained from Milli–Q water purification system (Millipore Corporation, Bedford, USA). Sulfate stock standard solution (500 mg/L) was prepared in Milli-Q water (free from sulfate) and used for further analysis. To establish the linearity of the method and standard addition quantification procedures, sulfate standard at different concentrations were prepared by weight. Solutions including collected water samples were filtered using a PTFE syringe filter (0.22 μm) (Macherey-Nagel GmbH, Düren, Germany) before being analyzed by UPLC method.

2.2. Analysis of water samples

Bottled drinking water samples from various sources were obtained from superstores based in Saudi Arabia. In this study, water samples from Metropolitan source were obtained from various cities supplied by the indigenous National Company (Saline Water Conversion Corporation, Saudi Arabia). Water samples were stored in the containers at 4 °C and all experiments were performed within a week to avoid microbial growth. Besides, blank and quality control (QC) samples were also studied in every sample set to ensure sample quality. Standard method has been used for the determination of sulfate in both bottled and metropolitan waters.

To assess the efficiency of the procedure and avoiding the influence of any matrix effects on compound peak intensity, retention time and shape, the sulfate quantification was performed by means of standard addition method which consist two non-spiked samples (zero levels) and four spiked samples 50% (5 μg/mL, concentration demonstrating the rise of sulfate in the sample next to spiking), 100% (10 μg/mL), 500% (50 μg/mL) and 1000% (100 μg/mL). All samples were analyzed in triplicates. The recovery rates were determined from the slope achieved while establishing the correlation between the added and found concentration of sulfate, and the statistical analysis was carried out using ANOVA method.

2.3. UPLC-MS/MS conditions

Ultra-performance liquid chromatographic separation of sulfate in water samples was performed by Acquity® UPLC method using n Acquity® BEH C_{18}reversed phase analytical column (Waters, Milford, USA). In this experiment, a guard-column (VanGuard™ BEH C_{18}, 1.7 μm) was applied during the sample analysis. The optimum separation of sulfate was acquired by means of mobile phase containing water (75%) and methanol (25%) in isocratic mode of elution and the flow rate was maintained as 0.2 mL/min. The experiment was run only for 2 min at ambient temperature. The column was also washed with a mixture of methanol and water (50:50, v/v) for 5 min at every 20 sample applications. The sample injection volume was 1 μL.

The triple quadrupole mass spectrometric detection of sulfate in water samples was carried out by Quattro Premier™ MS coupled with an electrospray ionization (ESI) source in the form of Z-spray. The source was operated in negative ionization method and the results acquisition was performed in Selected Reaction Monitoring (SRM) method. The ion transmission and fragmentation parameters were optimized by calibrating the equipment using sodium sulfate standard (10 mg/L). The target compound sulfate (SO_4^{2-}, m/z: 97) was analyzed as a precursor ion, and the product ion transitions SO_3^{2-} (m/z: 80) and SO_2^{2-} (m/z: 64) were used for quantification and confirmation, respectively. The optimal working parameters of the system were: source temperature (120 °C); capillary voltage (2.4 kV); desolvation temperature (250 °C); cone voltage (44 V); cone gas (60 L/h) and desolvation gas (600 L/h). Nitrogen gas (cone gas) was obtained from a nitrogen generator (NM30LA, Inchinann, United Kingdom), whereas, Argon (collision gas) was obtained from Specialty Gas Centre (Jeddah, Saudi Arabia). The vacuum of mass spectrometer was created using a rotary pump, Oerlikon, model SOGEVAC SV40BI (Paris, France). Table 1 demonstrates the SRM conditions used with the triple quadrupole mass spectrometric system. The results were processed using MassLynx V4.1 software (Waters, Milford, USA).

Table 1
Selected Reaction Monitoring conditions used with triple quadrupole method.[a].

Analyte	Precursor ion (*m*/*z*)	Quantification		Confirmation[b]	
		Product ion (*m*/*z*)	Collision energy (eV)	Product ion (*m*/*z*)	Collision energy (eV)
SO_4^{2-}	97	80	30	64	35

[a] Dwell time = 0.025 s.

[b] Confirmation ion intensity was higher than 10%.

3. Results and discussion

3.1. Analysis of water using an Ultra-performance liquid chromatography

In recent years, UP-LC method has been accepted as an innovative separation technique which permits for analysis and separation of small particles both speedily and efficiently (Swartz, 2005). The optimization of analytical parameters for water quality analysis using reversed phase chromatography is a significant task. In this method, small interactions between inorganic compound and a hydrophobic column were predictable. Indeed, sulfate content of water could not be eluted from the UP-LC system dead volume when only HPLC grade organic solvents was using as a mobile phase. Thus, the elution of sulfate was possible only with mobile phase containing either an aqueous or a mixture of both aqueous and organic phases. At first, the preliminary studies were performed on several hydrophobic columns containing stationary phases C_{18} and C_8. Besides, the column based on Hydrophilic Interaction Chromatography (HILIC) containing amide group stationary phase were also studied. Various mobile phases such as water, methanol and acetonitrile were studied either alone or a mixture of varied proportions at flow rate of the sample ranged from 0.1 to 0.5 mL/min. Also, the effect of the formic acid concentration (0.5%–1%) with mobile phase and sample injection volume (1 µL–5 µL) were also studied. Among the studied columns, the hydrophobic C_{18}has produced very nice symmetrical peak including low elution time of the target compound. Nevertheless, the hydrophilic HILIC and hydrophobic C_8were showed very poor results for instance peak tailing, higher elution time and peak split. The addition of organic modifier (formic acid) was also not improve the quality of peak and produced the similar results obtained during columns studies. However, in the previous study the addition of formic acid in mobile phase play an important role and offered Gaussian peak for bromate in drinking water samples (Alsohaimi et al., 2012). The effect of sample injection volume (1 µL – 5 µL) was also studied and the found very distinct results. Firstly, the sample was injected 5 µL and result showed that the sulfate was splitting in two peaks (Fig. 1). Thereafter, we start to reduce the sample injection volume under similar chromatographic conditions and attained very nice Gaussian peak at 1 µL (Fig. 1).

The standard chromatographic separation of sulfate in water samples was attained on reversed phase Acquity® BEH C_{18} column using mobile phase containing water (75%) and methanol (25%) in isocratic elution mode at the rate of 0.2 mL/min and sample volume was 1 µL. Relatively low flow rate and sample injection volume were found to be most favorable parameters for the determination of sulfate which showed effective ionic evaporation and desolvation in the ESI source of MS system, and a symmetrical peak to be well-defined as a minimum of fifteen scan points in their identification. The dead volume of the column was attained in 0.1 min which approved that the little interaction between inorganic compounds and column stationary phase. Therefore, the sulfate peak was acquired in less than 1 min in spite of applying lower flow rate. One of the main benefits of using low sized particle Acquity® BEH C_{18}column is that the column efficacy does not reduce while increasing the flow of the mobile phase.

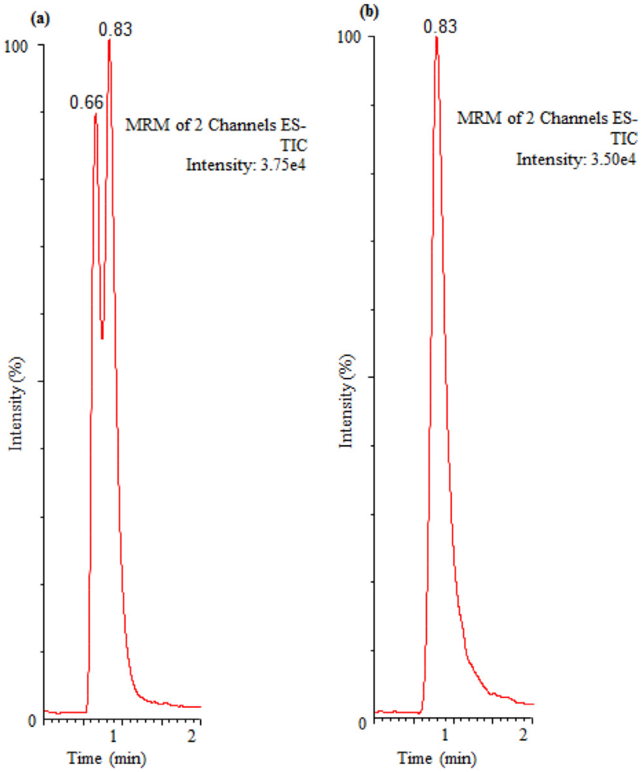

Fig. 1. Effect of sample injection volume (a) 5 µL and (b) 1 µL.

3.2. Optimization of mass spectrometric conditions

In order to enhance the analyte ion response, effective desolvation of mobile phase and reduce ion fragmentation, the ESI source parameters were studied. Initially, these conditions were validated by calibrating sulfate standard (10 mg/L) into MS system. The optimized conditions have been demonstrated in section 2.3. The experiments point out that the influence of conditions, source temperature, desolvation temperature, capillary voltage and desolvation gas exceeded maximum values, were insignificant. However, the influence of the cone voltage was noticeable on the identification of sulfate. The full scan mode of mass spectrum analysis was applied to select the most abundant sulfate ion, which correspond to *m*/*z* 97. The intensity of the sulfate ion was used to optimize the conditions involved in the process of ionization and transmission. The collision energy ranged from 5 V to 50 V were investigated to obtain the most abundant product ions, which result the loss of oxygen group from parent ion (*m*/*z*: 97) to two product ions SO_3^{2-} (*m*/*z*: 80) and SO_2^{2-} (*m*/*z*: 64). The MS/MS conditions and fragmentation pattern of target analyte have been demonstrated in Table 1 and Fig. 2, respectively.

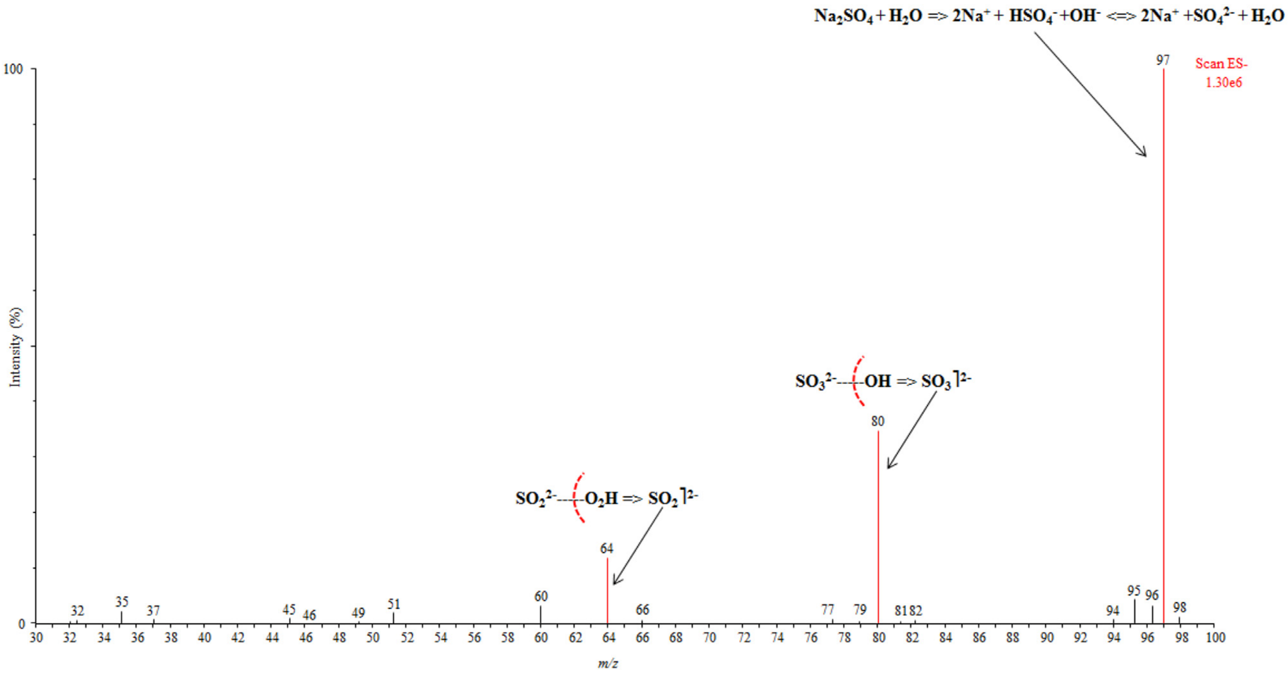

Fig. 2. Mass spectrometric fragmentation pattern of sulfate with plausible mechanism.

3.3. Validation of UPLC-MS/MS method

In this study, the quality parameters such as, instance linearity range, detection limit, quantification limit, precisions and accuracy were investigated to analyze the performance of this method. Under the optimal instrumental parameters, linearity of the method was assessed between concentrations range1 mg/L and 100 mg/L. The standard curve was obtained by plotting the amounts of seven calibration standards and the peak area. The calibration curve was linear over higher concentrations with excellent r^2 value ($r^2 = 0.999$). The outcome has shown the excellent correlation between peak area and sulfate concentrations.

The detection limit and quantification limits were determined as the sulfate concentration that formed a signal-to-noise ratio of 3:1 and 10:1, respectively. Detection and quantification limits were calculated by using a blank spiked with a low amount of sulfate. Excellent detection and quantification limits values were obtained (0.01 mg/L and 0.04 mg/L). These outcomes are closer than those previously reported using the flow-injection analysis, ion chromatography with UV detection techniques.

To assess run-to-run precision, six replicates of sulfate (0.5 mg/L) were analyzed in the same day while day–to–day precision, six replicates of standard solution were analyzed for three successive days. The values were measured based on the determination of RSD (%) of the peak area of sulfate. The day–to–day and run–to–run precisions for sulfate were achieved (3.46% and 1.97%). The obtained RSD values have demonstrated that the precision of the proposed method was good enough for the detection of sulfate in drinking water.

To validate the accuracy of the offered method, recovery values of the target compound were estimated by standard addition procedure. Thirty water samples from bottled and metropolitan have been analyzed and the recovery values were obtained from 93% to 97%. The influence of sample matrix has been observed at lower level and this could be to some extent due to the shape of ion source (Z–configuration), which usually not allowed the neutral compounds admittance in chromatographic and mass spectrometric systems. The obtained results revealed that the sample matrix doesn't alter the signal of analyzed compound in such kinds of samples and for quantitation purposes the external calibration method could also be used.

3.4. Sample analysis

The optimized UPLC-MS/MS method was used to analyze the sulfate concentration in bottled drinking water and metropolitan water samples. The sulfate content of the water samples was not affected by the sample matrix. Thus, the pre-treatment of water sample was not required prior to the UPLC-MS/MS analysis. Filtered water showed great benefit over conventional methods. In addition, the pre-treatment procedures for sample would greatly increase the materials and consumption of solvent, further losses of target analytes, sensitivity and longer analysis time.

Twenty-two bottled drinking water samples from different origins were obtained from Saudi Arabian markets, most of them were sterilized with ozone. Table 2 demonstrates the obtained sulfate concentration in bottled water samples. The sulfate concentrations were ranged from 3.31 mg/L to 76.22 mg/L. In most of the analyzed samples, the obtained sulfate concentrations were significantly different to the concentration claimed on label by the respective companies. The concentration of sulfate in samples 6, 7, 10, 12, 13, 15 and 22 was found to be similar with those claimed by the companies. However, in other samples the obtained concentration of sulfate was found to be nearly double than the concentration claimed by the companies. The concentration of sulfate in analyzed bottled water samples was found lower than the Secondary Maximum Contaminant Level (250 mg/L) (USEPA, 2009). The sulfate recovery rates in bottled water samples were obtained from 94% to 97%. The acquired UPLC-MS/MS chromatogram of sulfate in bottled drinking water (sample 22) has been displayed in Fig. 3. The peak is showing excellent symmetry, no tailing and no interfering ions with the target compound. To authenticate the cross contamination of the system, blank samples (Milli-Q water, free from sulfate) were analyzed after every real samples. The acquired UPLC-MS/MS chromatogram of Milli-Q water sample has been demonstrated in Fig. 4 which revealed that no any contamination

Table 2
SO_4^{2-} concentration in bottled drinking water samples achieved with UPLC – MS/MS method.

Bottled water	Water source	SO_4^{2-} (mg/L) ± SD	SO_4^{2-} claimed in the label (mg/L)	Disinfection process	Country of origin
Sample 1	–	23.76 ± 0.02	16	–	KSA
Sample 2	Well water	24.34 ± 0.02	30	Ozonation	KSA
Sample 3	–	28.75 ± 0.01	26	–	KSA
Sample 4	–	15.68 ± 0.02	30	–	KSA
Sample 5	–	24.13 ± 0.02	28	–	KSA
Sample 6	Well water	5.93 ± 0.03	5	Ozonation	KSA
Sample 7	–	13.35 ± 0.02	14	Ozonation	KSA
Sample 8	–	38.04 ± 0.01	51	–	KSA
Sample 9	–	3.31 ± 0.03	12	–	KSA
Sample 10	–	4.76 ± 0.03	5.40	–	Turkey
Sample 11	Well water	23.04 ± 0.02	32	Ozonation	KSA
Sample 12	–	21.40 ± 0.02	22	–	KSA
Sample 13	–	18.69 ± 0.02	18	Ozonation	KSA
Sample 14	Well water	19.17 ± 0.02	50	Ozonation	KSA
Sample 15	–	11.43 ± 0.03	12.60	–	France
Sample 16	–	36.21 ± 0.01	54	–	KSA
Sample 17	Well water	14.79 ± 0.02	22	–	KSA
Sample 18	Well water	72.09 ± 0.01	30	Ozonation	KSA
Sample 19	–	6.16 ± 0.03	10	–	KSA
Sample 20	–	12.07 ± 0.03	7	–	KSA
Sample 21	–	13.69 ± 0.03	20	–	KSA
Sample 22	–	76.22 ± 0.01	74.50	–	KSA

– not described; SD = standard deviation (n = 3); KSA = Kingdom of Saudi Arabia.

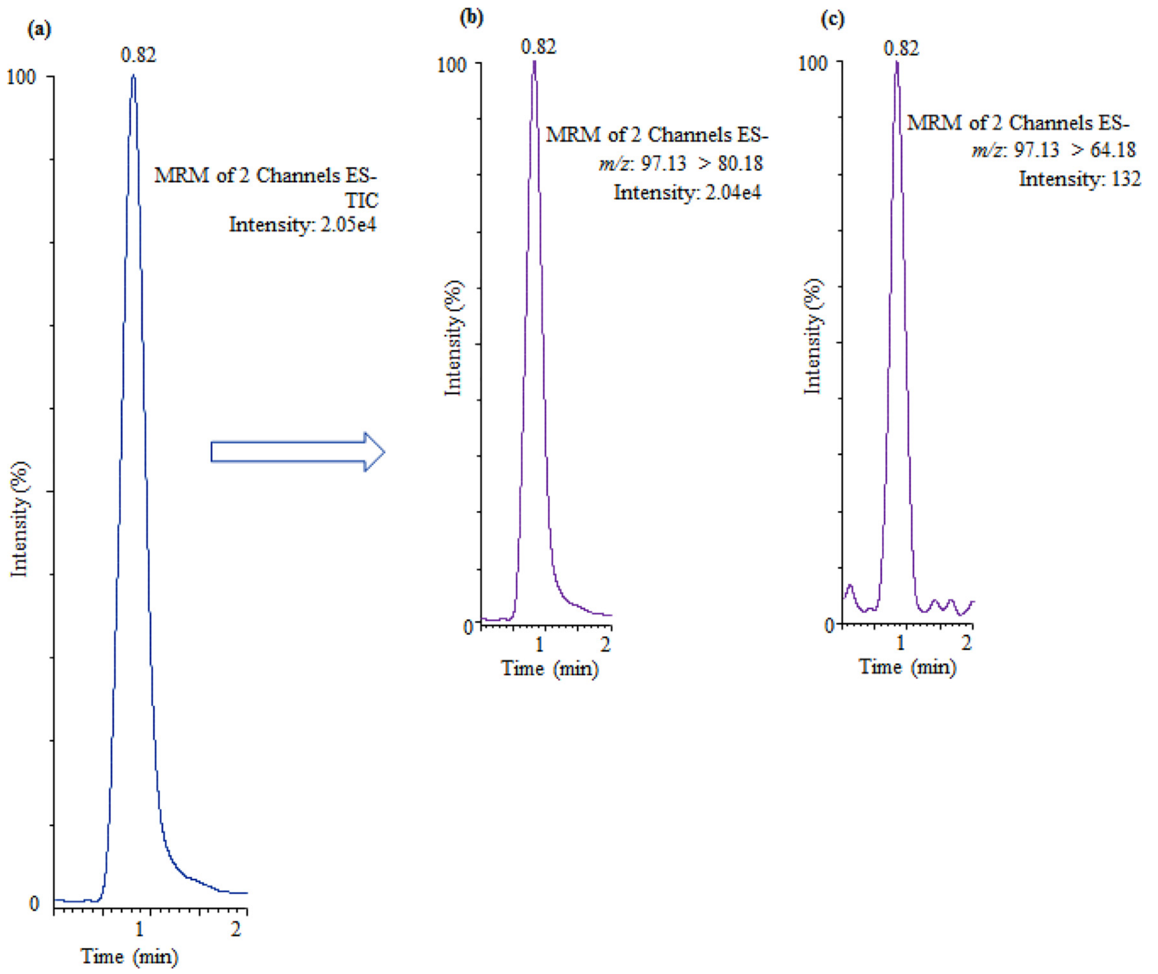

Fig. 3. UPLC-MS/MS chromatogram of sulfate in bottled drinking water (sample 22).

occurs during the analysis. The metropolitan water samples from different regions were also studied, and total eight metropolitan samples were analyzed and all of them were treated with hypochlorite. The achieved outcomes have been shown in Table 3. The sulfate levels were ranged from 36.78 mg/L to 268.42 mg/L. In all of the analyzed samples, the concentrations were significantly

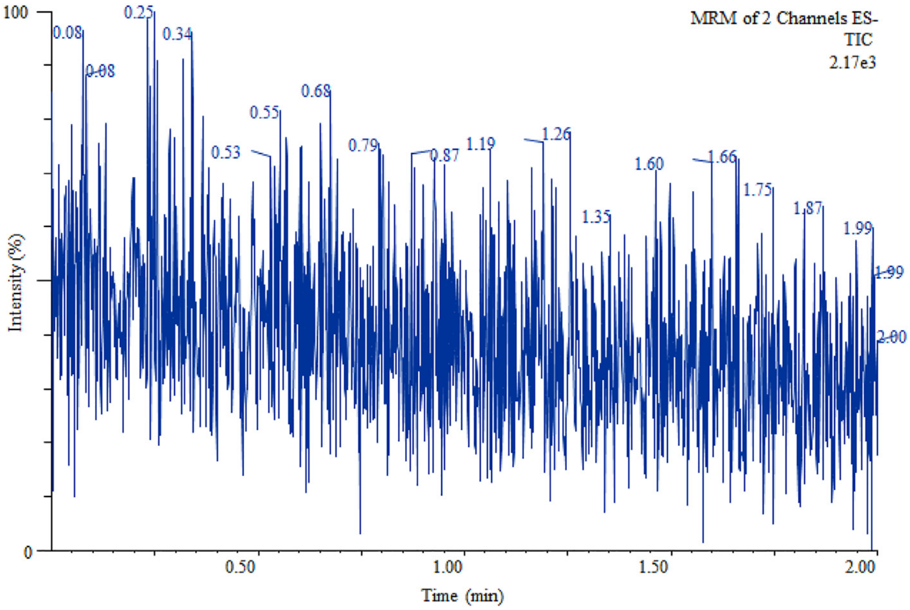

Fig. 4. UPLC–MS/MS chromatogram of blank sample (Milli-Q water, free from sulfate).

Table 3
SO_4^{2-} level in metropolitan water samples obtained with UPLC–MS/MS method.

Metropolitan water[a]	Water source	SO_4^{2-} (mg/L) ± SD	Disinfection process
Sample 1	Desalinated + well water	82.91 ± 0.03	Chlorination
Sample 2	Desalinated + well water	268.42 ± 0.01	Chlorination
Sample 3	Desalinated + well water	151.31 ± 0.01	Chlorination
Sample 4	Desalinated water	102.78 ± 0.02	Chlorination
Sample 5	Desalinated water	96.85 ± 0.02	Chlorination
Sample 6	Desalinated water	82.68 ± 0.03	Chlorination
Sample 7	Desalinated water	142.23 ± 0.01	Chlorination
Sample 8	Desalinated water	36.78 ± 0.04	Chlorination

[a] Samples from various location in KSA; SD = standard deviation (n = 3).

different. The highest concentration of sulfate (268.42 mg/L) was obtained in sample 2 and this content was higher than that of prescribed limit for drinking water (250 mg/L) (USEPA, 2009). The sulfate recovery rates were obtained from 93% to 96%. In comparison to bottled drinking water, metropolitan water samples contained higher amounts of sulfate. The results obtained from this study are the source of data relating to the availability of sulfate in bottled and metropolitan water samples from Saudi Arabia.

4. Conclusion

A novel technique based on UPLC–MS/MS was proposed to assess sulfate content in bottled and metropolitan water collected from various provinces of Saudi Arabia. The optimized procedure has illustrated to be faster with less than one-minute sample analysis time. Excellent detection and quantification limits values were achieved, and precise with excellent run–to–run precision and day–to–day precision values. The excellent quality parameter values and insignificant matrix effects achieved during analysis have made favorable to analyze sulfate in water samples, and offered advantages over conventional techniques and rigorous sample preparation. The performance of proposed method along with the achieved results from analyzed water samples make favorable to propose a novel method for the routine study of sulfate content in drinking water. The achieved data from this work could be applied to estimate the sulfate intake by individuals in Saudi Arabia, and therefore to advance the water quality and security.

Declaration of competing interest

The authors declare that they have no any conflict of interest.

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