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A new method of analysis of peroxydisulfate using ion chromatography and its application to the simultaneous determination of peroxydisulfate and other common inorganic ions in a peroxydisulfate matrix

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ABSTRACT

A new method for the determination of peroxydisulfate using ion chromatography has been developed. Elution of peroxydisulfate was effected by isocratic elution using 200 mM NaOH at 40 °C. A modification of the method using gradient elution was able to simultaneously determine other common inorganic ions (nitrate, nitrite, sulfate and chloride) down to significantly low concentrations in a peroxydisulfate matrix. The relative standard deviations (RSD) were in the range of 0.5–5%, for peak areas and <0.2% for peak retention times. The recoveries were between 95% and 120% for a concentration range of about 0.5–42 ppm. The limit of detection for peroxydisulfate ion was 0.2 ppm and for the other ions were $\leq 2 \times 10^{-2}$ ppm. The calibration curves were linear with slope and intercepts close to 1 and 0, respectively.

1. Introduction

The peroxydisulfate anion ($S_2O_8^{2-}$) is a strong oxidizing agent with oxidation potential of 2.01 V. Being kinetically slow in its original form, it oxidizes via dissociation into reactive radicals ($SO_4^{\bullet-}$ and $OH^{\bullet}$) with the end products of SO_4^{2-} and SO_5^{2-} ions. Activated peroxydisulfate has found use in various applications including initiators and curing agents in polymerization, surface preparation for plating and coating processes, preparation of adhesives, measurement of total organic carbon (TOC) and many others [1–4]. Because of its stability prior to activation, the use of peroxydisulfate is also becoming increasingly popular in the in situ chemical oxidation (ISCO) for decontamination of groundwater. This involves activating peroxydisulfate directly at a contaminated source zone in order to oxidize contaminants into harmless end products within the soil matrix. This process requires monitoring peroxydisulfate concentration in groundwater over time. In one of our recent studies, we have used sodium peroxydisulfate for the removal of nitric oxide (NO), where a simultaneous determination of chloride, nitrite, nitrate, sulfate and peroxydisulfate was necessary [5].

A number of methods for the determination of peroxydisulfate have been reported in the literature. These include reductometric [6–9], polarographic [10–13], spectrophotometric [3,14,15], chemiluminescence [16] and ion-pair chromatography [17,18] methods. Unfortunately, all of these methods suffer from some form of drawbacks of being complex, tedious and time consuming and thus have the possibility of introducing significant amount of errors in the experimental steps. For example, among the reductometric methods, iodometry and ferrometry both involve a back-titration step after the redox reactions with peroxydisulfate. The polarographic methods also involve many steps and are thus complex and tedious. As an additional problem, the determination of peroxydisulfate using iodometric method has been shown to be affected by the presence of even trace quantities of nitrite and dissolved NO [8], which are common in some aqueous systems subjected to peroxydisulfate oxidation. The spectrophotometric methods [3,15] eliminate the back-titration step required in the reductometric methods. However, they still involve a number of time-consuming steps and quite a few chemicals, and the reaction times are also large (30–40 min). The method by Shiundu et al. [14] and De Oliveira et al. [13] require a flow injection analysis setup. They are also very fast and efficient in processing a large number of samples to detect a single species but is not suitable for detecting several ionic species at the same time. Weidenauer et al. [17,18] have described ion-pair chromatographic methods to separate the S-anions (specifically dithionate, peroxydisulfate and tetrathionate) using a LiChropher-100CH column with tetrabutylammonium hydroxide (TBAOH) as the ion-pairing

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agent. However, the applicability of this method to the simultaneous determination of common anions with peroxydisulfate is doubted. The stationary phase in ion-pair chromatography is non-ionic and separation is sensitive towards the ion-pairing agent used. While ion-exchange chromatography separation could be achieved simply by changing the concentration of the same eluent, entirely different ion-pairing agents may be needed for the separation of different species involved. In fact, in addition to the ion-pair chromatography they have used ion-exchange chromatography to separate the rest of the S-anions (sulfite, sulfate, thiosulfate and thiocyanate).

To the best of our knowledge, determination of peroxydisulfate using ion chromatography has not been reported in the literature. This paper presents a method developed for the simultaneous determination of the common inorganic ions such as chloride, nitrite, nitrate, sulfate and peroxydisulfate using ion chromatography. It is simple, reliable, fast, accurate and requires the least human intervention. The parameters have been optimized for best peak shape and resolution, and the determination of low quantities of nitrate and nitrite in a high peroxydisulfate matrix. A certain amount of sulfate inevitably exists in an aqueous solution of peroxydisulfate because of its decomposition. However, the amount of sulfate is quite low in a freshly prepared peroxydisulfate solution and it can easily be taken into account while calibrating the method for peroxydisulfate. This method uses both internal and external eluent generation for best results.

2. Materials and methods

2.1. Chemicals

Deionized (DI) water with specific resistance ≥18.2 MΩ at 25 °C, purified using a Milli-Q Advantage A10 with Elix 5 system (Millipore, Bedford, MA) was used for the preparation of all samples, standards and eluents. Sodium hydroxide pellets (certified ACS reagent) for the preparation of external eluents, was obtained from Fisher Scientific (Pittsburgh, PA). Sodium peroxydisulfate powder (98+%) for making calibration and validation standards, and methanol (99.8%, ACS reagent grade) were obtained from Acros Organics, New Jersey, NJ. Primary chloride, nitrite, nitrate, sulfate and phosphate standards (100 μg/L and 1000 μg/L) were obtained from High Purity Standards, Charleston, SC. All secondary standards and eluents were freshly prepared before use.

2.2. Instrument

The chromatography system consisted of a Dionex ICS-3000 Reagent-Free Ion Chromatograph (Dionex Corporation, Sunnyvale, CA) with dual pump (DP; gradient/isocratic), an eluent generation system (EG40), a detector compartment (DC) with conductivity detectors and an autosampler (AS40). The eluent generator contains an EGC KOH with continuously regenerated trap columns (CR-TC) for removing contaminant ions. The separations were performed with Dionex IonPac AS11-HC (4 mm × 250 mm) analytical column and IonPac AG11-HC (4 mm × 50 mm) guard column with anion self-regenerating suppressor (ASRS 300) in the autosuppression recycle mode of operation and a 25-μl sample loop. Dionex Chromeleon v. 6.8 was used for instrument control, data collection and processing. Internal eluent generator cartridge was only capable of going up to 100 mM KOH at 1 ml/min flow rate and NaOH solution was used as external eluent for higher concentrations. Since NaOH solution picks up carbon dioxide from air when left standing for a long period, the solution to be used as eluent was prepared fresh each day and the headspace was filled with nitrogen.

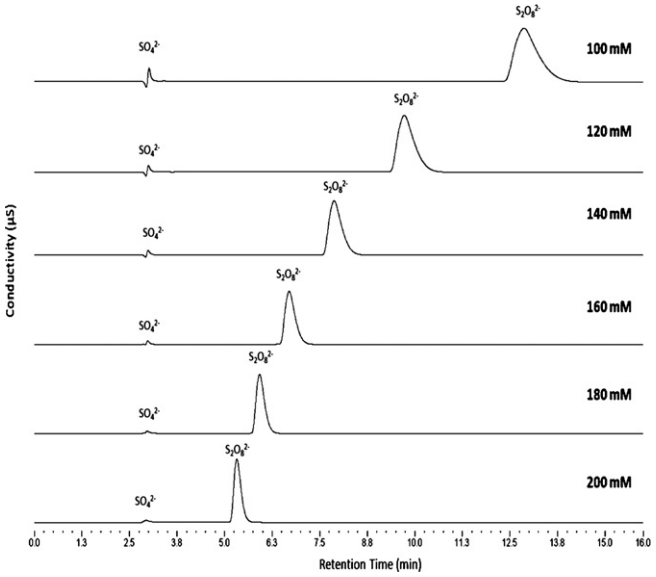

Fig. 1. Chromatograms of peroxydisulfate samples obtained at different eluent concentrations (peroxydisulfate concentration = 100 mg/L).

3. Results and discussion

3.1. Column selection

The IonPac AS11-HC with hydroxide elution is used in our laboratory for the routine analysis of the common inorganic ions. It is able to resolve a large number of inorganic anions in complex matrices like chemical wastewater effluents [19] as well as drinking and ground water [20]. Also, hydroxide elution is able to separate both weakly retained and strongly retained ions. This system has been extended to the analysis of peroxydisulfate since our search of the open literature did not reveal any discussion about the use of ion chromatography for the separation of peroxydisulfate.

3.2. Optimization of separating conditions

Optimization of separation conditions for best retention time and peak shape is necessary for the quantification of peroxydisulfate. Peroxydisulfate is a strongly retained ion due to its large size and its high negative charge (−2). Indeed, below an eluent concentration of 100 mM NaOH it was observed that peroxydisulfate did not elute in 30 min. At the same time, the highest possible concentration of NaOH to be suppressed by the ASRS 300 suppressor was 200 mM. Therefore, elution of peroxydisulfate was tested at different eluent concentration between 100 mM and 200 mM NaOH. Fig. 1 shows the chromatograms obtained at different eluent concentrations and Fig. 2 shows the variation of retention time and tailing factor with NaOH concentration at 35 °C. The peroxydisulfate peaks were tailed and asymmetric. However, a high concentration of eluent causes decrease in tailing factor and retention time; the peaks are also sharper at higher eluent concentration. Therefore the highest possible eluent concentration, i.e. 200 mM NaOH (external eluent), was chosen for the analysis of peroxydisulfate. The highly asymmetric nature of the peroxydisulfate peak was an important consideration since it could induce quantification errors. A value between 1.2 and 2 (USP standard) is generally acceptable [21].

Column temperature also has a considerable effect on peak shape, several runs were made over the temperature range of 20–40 °C using isocratic condition of 200 mM NaOH. The suppressor was connected outside the detector compartment (DC) so that

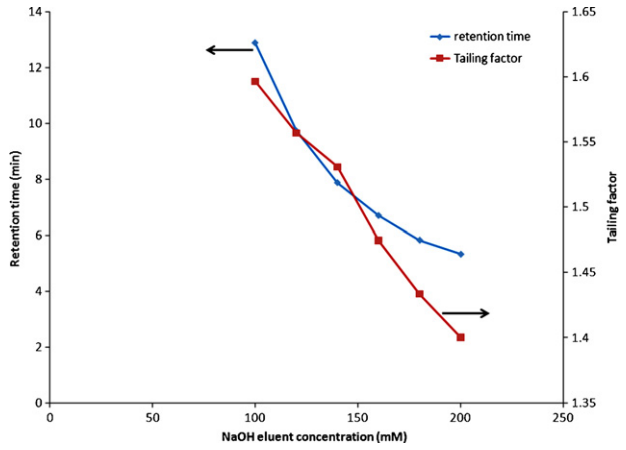

Fig. 2. Change in retention time and tailing factor of the peroxydisulfate peak with eluent concentration (peroxydisulfate concentration = 100 ppm).

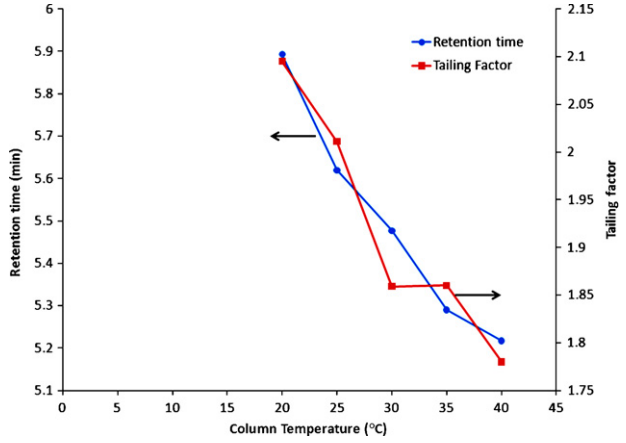

Fig. 3. Variation of retention time and tailing factor of the peroxydisulfate peak with column temperature (eluent concentration = 200 mM NaOH, peroxydisulfate concentration = 500 mg/L).

the suppression performance does not vary with the change of compartment temperature and it was recommended by Dionex that the suppressor not be operated above a temperature of 35 °C [22]. Fig. 3 shows how retention time and tailing factor of peroxydisulfate peaks varied with column temperature. In general, the peaks were more symmetric and eluted faster at high temperatures. Column temperature of 40 °C resulted in the lowest values of tailing factor (about 1.5) and retention time. Peroxydisulfate elution was also tested using methanol. Unfortunately, above 60 mM NaOH, presence of methanol caused the background conductivity to increase significantly which the suppressor was unable to suppress. Therefore, using methanol with high NaOH concentration in the eluent was not feasible. However, peroxydisulfate elution was tested with 5% methanol in 60 mM NaOH but it did not elute in a 30 min run. Therefore, further investigations with methanol were suspended.

Although a high eluent concentration is suitable for peroxydisulfate analysis, the same is not true for the common inorganic anions such as chloride, nitrate, nitrite, sulfate. A good resolution of these anions is not obtained at high concentration isocratic elution. Therefore, a change in the elution conditions is necessary to analyze these common ions simultaneously with peroxydisulfate. In the initial part of the run low concentration (<20 mM KOH–internal eluent generation) was used to elute chloride, nitrate, nitrite and sulfate. Subsequently, the eluent concentration was increased to 180 mM NaOH (external eluent) + 18 mM KOH (internal eluent) to elute the peroxydisulfate. The conditions of analysis are presented in Table 1.

Table 1
Gradient elution conditions to separate chloride, nitrite, nitrate, sulfate and peroxydisulfate anions.

Time (min)	Internal eluent (KOH) Conc. (mM)	External eluent (1.0 ml/min)	
		%A (NaOH, 200 mM)	%B (DI-Water)
−5–0 (equlibration)	18	0	100
0 (injection)	18	0	100
0–6	18	0	100
6–10 (gradient)	18	From 0 to 90	From 100 to 10
10–15	18	90	10
15–18 (gradient)	18	From 90 to 0	From 10 to 100
18–25	18	0	100

Moreover, since the concentration of eluent was increased quite quickly it is necessary to correspondingly change the suppressor current to prevent a sudden jump in conductivity. The current settings of the suppressor used during the run are shown in Table 2. They correspond to the times given in Table 1.

The conditions for the initial isocratic elution are important for the good resolution of nitrate from sulfate. The small amount of sulfate that is invariably present in peroxydisulfate solution also elutes during this phase, which interferes with the analysis of the other ions present in even smaller quantities, chiefly nitrate. It has been observed that the retention times of nitrate and sulfate are close together and their position relative to each other changes with the change of temperature and eluent concentration. The effect of temperature on the elution of different anions has been discussed extensively by Hatsis and Lucy [23]. It was shown that changing temperature causes changes in retention time as well as selectivity of the different ions based on their charges. In this study we found that at low temperatures the peaks elute sooner than at higher temperatures. A high eluent concentration also causes the peaks to elute sooner and close to each other. Consistent with Hatsis and Lucy's [23] work, selectivity changes have been observed between nitrate and sulfate depending on the temperature. For example, at a particular eluent concentration (e.g. 20 mM KOH) sulfate peak might occur after nitrate at higher temperatures and before nitrate at lower temperatures. It is preferable to use higher eluent concentration since the peaks are sharper which improves their S/N ratio and makes their quantification better. However, it is also preferable to have the sulfate elute after the nitrate so that its tail does not interfere with the measurement of the nitrate peak. For these reasons, a higher temperature of 40 °C and eluent concentration of 18 mM is chosen for the initial isocratic elution of the common inorganic ions, which gives a good resolution of all the peaks while still eluting the nitrate ion earlier than sulfate. The higher temperature also has the added advantage that the peroxydisulfate peak is sharper and less asymmetric. A representative chromatogram obtained using the conditions described is given in Fig. 4.

The calibration has been performed using two batches of 7 standards prepared independently with different concentration ranges of the ions. Three injections were made for one sample in a batch, making a total of 6 injections at a particular concentration. The response measured was the area under the peak. The average of

Table 2
Suppressor current changes corresponding to the gradient elution in Table 1.

Time (min)	Current (mA)
−5 to 10	50
10	100
25	200
12–25	500
25	50

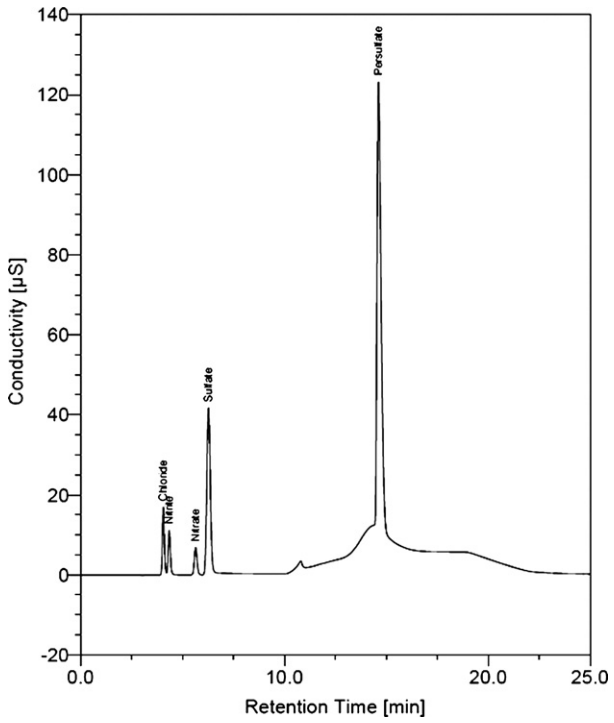

Fig. 4. A representative chromatogram obtained using this method.

6 injections were plotted against the introduced concentration of the ions and regressed to find the slope and the intercept of the calibration curve. The following section describes the validation and characterization of this method based on the calibration performed.

3.3. Method validation and characterization

The following steps are followed for the validation and characterization of this chromatographic method as suggested by the USP [24]: (a) accuracy, (b) precision, (c) linearity, (d) limit of detection and (e) limit of quantification. The selectivity of the method is also important. The minimum resolution in our case was obtained between the chloride and nitrite peaks. However, the resolution between these two peaks was never less than 1.5, which was acceptable. The resolution between nitrate and sulfate was also quite good (>2).

3.3.1. Accuracy

The accuracy of analysis of peroxydisulfate was evaluated by comparing the values obtained using this method against an established method. The spectrophotometric method described by Liang et al. [15] was used for this purpose. Peroxydisulfate used in ISCO for groundwater remediation mainly target volatile organic compounds (VOC). Therefore, mixtures were made containing some of the common VOCs, benzene, toluene, phenol, 1,1,1-tricholoroethane, iso-butyl benzene and xylene (each having a concentration of 1 μg/L), and four different concentrations of peroxydisulfate. These were analyzed using both the methods and

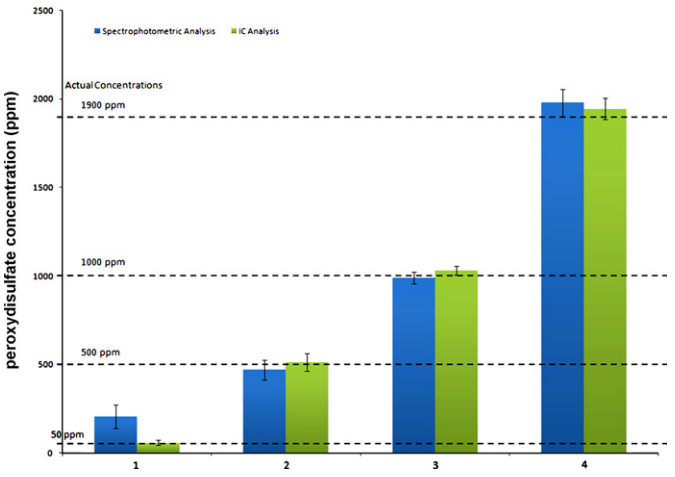

Fig. 5. Comparison of peroxydisulfate concentration obtained using this ion-chromatographic method with a previously established method.

the results are compared in Fig. 5. Both methods are able to quantify peroxydisulfate quite well and in fact, at low concentration the ion-chromatographic method performs better.

Spike-recovery experiments were performed to find out the accuracy of the method for the other ions. Mixtures containing the VOCs mentioned above and high concentration of peroxydisulfate (1000 ppm) were spiked with two different concentrations of nitrate, nitrite, chloride and sulfate. Concentrations of the ions were determined using the calibration obtained previously. The introduced and measured concentrations are presented in Table 3.

3.3.2. Precision

The precision of the method for all the ions was evaluated by making repeated analyses of a fixed concentration of each ion on different days. The concentrations used for the evaluation of precision of the different ions are about 8 ppm for chloride, 3 ppm for nitrate and nitrite, 15 ppm for sulfate and 50 ppm for peroxydisulfate. Two independent batches were prepared each day and each was injected 4 times thus making a total of 8 injections ($n = 8$) at a particular concentration. This was repeated through three days ($N = 3$) and the relative standard deviations (RSD) were calculated. The responses measured were the retention times and the area under the peak. The intra-day RSD (Eq. (1)) was calculated from the standard deviation of the injections on a day (σ_r) and the day average ($\bar{x}_i$) and the day-to-day RSD was calculated from the standard deviation of the day averages (σ_d). These values are presented in Table 4. The retention time dispersions of all the ions were quite insignificant (<0.2%). This indicates that there is very little interference among the ions. It was noted during the experimentation that the maximum variation of retention times between two samples (of similar concentration) injected with an interval of about 60 days and with a new suppressor was about 5%. The area precisions were also very good (<3%), except for day-to-day dispersion of peroxydisulfate, which was a little over 5%. This is still acceptable and

Table 3
Spike-recovery analysis for the common anions.

Anionic species	Spiked concentration (ppm)	Measured concentration (ppm)	Recovery (%)	Spiked concentration (ppm)	Measured concentration (ppm)	Recovery (%)
Chloride	2.14	2.23	104.2	28.57	28.38	99.3
Nitrite	0.57	0.60	105.3	8.57	8.36	97.5
Nitrate	0.57	0.68	119.3	8.57	9.52	111.1
Sulfate	9.11	8.91	97.8	42.1	41.34	98.2

Table 4
Dispersion of peak retention times and peak areas within a day and from day to day.

Anionic species	Area		Retention time (min)	
	RSD (%) intra-day	RSD (%) day-to-day	RSD (%) intra-day	RSD (%) day-to-day
Chloride	0.8	0.6	0.001	0.06
Nitrite	1.9	1.7	0.02	0.02
Nitrate	1.9	2.4	0.03	0.09
Sulfate	1.9	2.7	0.04	0.15
Persulfate	2.5	6.2	0.04	0.07

Table 5
Linearity of the method.

Ions	Range (ppm)	Slope confidence interval	Intercept confidence interval	R^2
Chloride	2–29	1.0070 ± 0.0027	−0.0080 ± 0.014	0.9998
Nitrite	0.5–9	1.1 ± 0.025	−0.047 ± 0.027	0.9999
Nitrate	0.5–9	1.1 ± 0.025	−0.016 ± 0.028	0.9988
Sulfate	3–50	1.00 ± 0.016	−0.56 ± 0.200	0.9986
Persulfate	50–1900	1.0 ± 0.033	6.7 ± 0.92	0.9999

Table 6
Limits of detection for this method.

Anionic species	Detection limit (ppm)
Chloride	2×10^{-3}
Nitrite	2×10^{-2}
Nitrate	2×10^{-2}
Sulfate	2×10^{-2}
Persulfate	0.2

is expected to be much better if the calibration range is narrowed.

$$\mathrm{RSD}_{\text{intra-day}}\,(\%) = \frac{\sigma_r}{x_i} \times 100 \quad (1)$$

$$\mathrm{RSD}_{\text{day-to-day}}\,(\%) = \frac{\sigma_d}{\bar{x}} \times 100 \quad (2)$$

$$\sigma_d = \frac{\sum_{i=1}^{N} (\bar{x}_i - \bar{x})^2}{N} \quad (3)$$

3.3.3. Linearity

The linearity of the method was evaluated by plotting concentrations obtained by applying the method against introduced concentrations for each ion. Solutions containing different concentrations of the ions in the calibration range were analyzed and their concentrations were calculated using the calibration slopes and intercepts obtained previously. The calculated concentration was regressed against the actual concentration. If the method is linear and accurate, the slope and intercept of these regressions should be 1 and 0, respectively. Table 5 presents the slope and intercept confidence intervals (95%), the range of analysis and the coefficient of determination for the linear regressions. Coefficients of determination greater than 0.998 have been obtained for all the species and the slopes and the intercepts are not significantly different from 1 to 0, indicating a very strong linearity of the method.

3.3.4. Limit of detection and quantification

A simple procedure was adopted for estimating the limits of detection and quantification. Seven samples with increasing dilutions (from 20 to 2×10^{-5} ppm of each ion) were analyzed successively. The concentration immediately before which the S/N ratio becomes ≤3 was taken as the detection limit. The quantification limit was simply 3 times the detection limit. The limit of detection and the S/N ratios are presented in Table 6.

4. Conclusion

The proposed ion chromatographic method for the determination of peroxydisulfate measurement is fast, accurate and simple relative to other methods. Moreover, this method, or a modification of it, may be used for the simultaneous determination of various other ions obviating the need for using different methods for different species. It shows a very good linear correlation for peroxydisulfate as well as for nitrate, nitrite, chloride and sulfate with less than 5% deviation from the theoretical values. Although in its present form it is able to quantify these five ions very well there is still room for subsequent improvements in terms of using different columns, eluents and separation conditions, etc. These improvements will be the subject of future studies. This study is intended to present a new, simple and reliable method for peroxydisulfate analysis and a first step towards analyzing peroxydisulfate using ion chromatography.

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