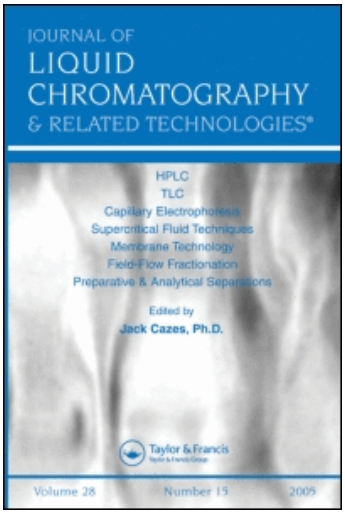

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Simultaneous Determination of Trace Oxoanions Using Ion Chromatography With Ultraviolet Absorbance Detection

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SIMULTANEOUS DETERMINATION OF TRACE OXOANIONS USING ION CHROMATOGRAPHY WITH ULTRAVIOLET ABSORBANCE DETECTION

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ABSTRACT

CS5A column had bifunctional (cation exchange / anion exchange) stationary phase. It was the first time that CS5A column was used for the analysis of trace oxoanions by ion chromatography. The influence of sodium phosphate concentration, methanol concentration, and eluent pH on their separations were studied. An eluent of 7.5 mM Na_2HPO_4, pH 9.3 was found to be the most suitable for the analysis of SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, GeO_3^{2-}, and CrO_4^{2-} simulanteously. An eluent of 0.75 mM Na_2HPO_4, pH 9.3 was found to be the most suitable for the analysis of IO_3^-, $H_2AsO_3^-$, BrO_3^-, NO_2^-, and NO_3^- simulanteously. The detection method

employed was selective and direct UV absorbance at 204 nm was utilized. Several other anion separation columns (AS4A-SC column, AS9-SC column, AS11 column, and PAX 500 column), which had different structures and properties, were compared to CS5A column. Among them, CS5A column was the best choice.

INTRODUCTION

Oxoanions were widely spread throughout the environment as a result of fuel consumption, industrial, agricultural, and natural processes.[1] Many of them, such as chromate, tungstate, molybdate, selenite, selenate, arsenite, arsenate, germanate, nitrite, nitrate, iodate, and bromate have been recognized as dangerous or potentially dangerous pollutants.[1,2]

It was well known that some of them were essential for biological systems, both as a nutrient and as a potential toxicant, the difference between the necessary daily intake and the toxical value was narrow, such as selenium and germanium.[3] Moreover, speciations of different chemical forms were particularly important, as the toxicity and the bioavailability depended on their chemical forms, such as selenite, selenate, arsenite, arsenate, nitrite, and nitrate.

Since the 1970s, the advance of ion chromatography provided a sensitive tool for multi-anions analysis. The method for the determination of Se, Mo, As, and Cr as their oxoanions under alkaline condition using carbonate as the elution has been developed.[2,4-8] But, when determined by conductance, the analyte whose PKa was more than 7 could not be detected because the conductance of effluent was measured in a neutral or acidic solution.

As most of the oxoanions had strong UV absorbance in the range of 195-220 nm, a procedure for direct spectrophotometric determination were suitable for the analysis of these oxoanions.[9,10] The absorption wavelength could be carefully selected to achieve the required selectivity and sensitivity. Moreover, some previous method could only be capable of differentiating a few oxoanions.

As for more oxoanions, they could not be well separated. Thus, it was necessary to find a reliable method for the analysis of more oxoanions simultaneously.

In this paper, five anion analytical columns with different properties (CS5A column, AS4A-SC column, AS9-SC column, AS11 column, and PAX 500 column) were studied. Among them, CS5A column was the best choice. It had special ability of separation.

The influence of Na_2HPO_4 concentration, methanol concentration and eluent pH on the separation was investigated. By using two Na_2HPO_4 concentrations, all the oxoanions could be well separated.

EXPERIMENTAL

Instrumentation

Chromatographic analyses were performed on a metal free Dionex DX-300 ion chromatograph (Dionex Corp., Sunnyvale, CA, U.S.A) equipped with advanced gradient pumps (AGP), a high pressure injection valve with a 60 µl sampling loop, and a Dionex UV-Vis variable wavelength detector.

Chromatographic columns included an IonPac CG5A guard column and an IonPac CS5A analytical column, an IonPac AG4A-SC guard column and an IonPac AS4A-SC analytical column, an IonPac AG9-SC guard column and an IonPac AS9-SC analytical column, an IonPac AG11 guard column and an IonPac AS11 analytical column, a MPIC-NG1 guard column and an OmniPac PAX-500 analytical column.

Data collection and operation of all components in the system were controlled by Dionex AI-450 chromatographic software interfaced via an ACI-2 advanced computer interface to an AST Power Premium 3/33 computer.

Reagents and Standards

All chemicals used in this study were of analytical reagent grade reagents. Water was deionised before use. The stock solutions of standard oxoanions (1000 ppm) were prepared by dissolving appropriate amounts of sodium or potassium salts in deionised water and stored in glass containers. Working standard mixture solutions of oxoanions were prepared by diluting the stock solutions as required.

Ion Chromatographic Procedure

Eluent was prepared by dissolving sodium phosphate in 1 L of deionised water. The pH of the eluent was adjusted by NaOH solution. Then, filtered through a 0.45 µm member filter and degassed by nitrogen before use. The flow rate was normally set at 1 ml min^{-1} or as stated. All operations were carried out at room temperature.

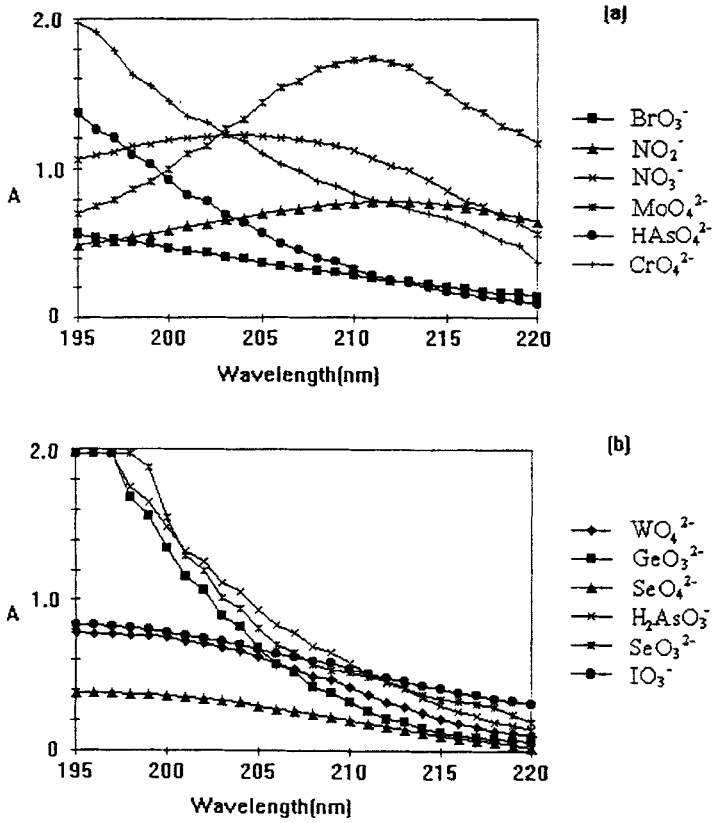

Figure 1. Absorbance spectra of oxoanions in the range of 195-220 nm.

RESULTS AND DISCUSSION

Choice of Wavelength

Conventionally, electrical conductivity detectors were usually used to detect inorganic anions. But, it was not suitable for some oxoanions whose PKa were more than 7. It was known that many oxoanions had suitable chromophores.[11]. SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, GeO_3^{2-}, CrO_4^{2-}, IO_3^-, $H_2AsO_3^-$, BrO_3^-, NO_2^-, and NO_3^- had appreciable absorption in the range of 190-220 nm. So, these oxoanions could be detected in this wavelength range. Fig.1(a) and (b) showed their UV absorbance spectra. The lower oxidation states of As and Se exhibited relatively greater absorbance. The shorter

wavelength was, the higher absorbance for most oxoanions. But, when the wavelength decreased, the background absorbance would increase and the signal-to-noise values would also increase. This decreased the sensitivities of detection. The wavelength which was chosen was 204 nm.

Choice of Analytical Column

One of the important aims of this work was to choose a suitable analytical column for the separation of oxoanions. It was well known that degrees of the latex cross-linking and types of functional groups attached to the latex beads acted as important roles for the selectivity of separation. They affected the distribution equilibrium between analyte and eluent directly. At present, there were many different anion analytical columns with diverse selectivities which were available from Dionex. Five of them were chosen to evaluate inorganic oxoanions assay. Their structural and technical characteristics were summarized in Table 1.

Table 2 showed the elution time of each oxoanion at their optimum eluent conditions. It was evident that the elution order of oxoanions, which were separated exclusively via anion exchange processes, could not be altered.

IonPac CS5A column was usually used for the separation of cations and had never been used for the separation of oxoanions. It had two kinds of functional groups (anion and cation exchange sites). Both of them had low hydrophobicity. It was well known that anions could be separated on the anion functional groups. When oxoanions were separated on the anion functional groups (alkanol quaternary ammonium), the cation functional groups (sulfonic acid) had special synergistic effects. This would result in better separations.

While using CS5A column, the suitable eluents were 7.5 mM Na_2HPO_4, pH 9.3 for the analysis of SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, GeO_3^{2-}, and CrO_4^{2-}, 0.75 mM Na_2HPO_4, pH 9.3 for the analysis of IO_3^-, $H_2AsO_3^-$, BrO_3^-, NO_2^-, and NO_3^-. Fig.2(a) and (b) showed their chromatograms. All these analytes were well separated.

The CS5A analytical column significantly facilitated the analysis of polarizable oxoanions, such as WO_4^{2-}, MoO_4^{2-}, CrO_4^{2-} and NO_3^-. Reducing the hydrophobicity of the functional groups bound to the latex beads, which minimized adsorption phenomena, made it possible to elute polarizable oxoanions. The peaks broadening could be greatly reduced. On the other hand, it had strong interaction with hydrophilic oxoanions, such as IO_3^-, $H_2AsO_3^-$ and BrO_3^-, and they were well separated, especially with the synergistic effect from cation functional groups.

Table 1

Structural and Technical Properties of Four Analytical Columns

Column	Particle Diameter (μm)	Substrate %X-Linking	Latex Diameter (μm)	Latex %X-Linking	Capacity (ueq/col)	Functional Group	Hydrophobicity
AS4A-SC	13	55	160	0.5	2.0	Alkanol QA	medium-low
AS9-SC	13	55	110	20	30-35	Alkyl QA	medium
AS 11	13	55	85	6	45	Alkanol QA	very low
CS 5A		9	55				
		Anion:	76	2	40	Alkanol QA	low
		Cation:	140	10	20	Sulfonic acid	low
PAX 500	8.5	55	60	4	40	Alkanol QA	low

QA: Quaternary ammonium

Table 2

Elution Time of Oxoanions on the Four Columns

	PAX 500* (min)	CS5A (min)	AS4-SC (min)	AS9-SC (min)	AS11 (min)
IO_3^-	3.08	1.99	2.10	1.65	1.88
$H_2AsO_3^-$	3.22	2.56	2.28	1.79	2.37
BrO_3^-	4.02	3.05	3.42	2.40	3.57
NO_2^-	5.55	4.01	4.80	3.32	4.55
NO_3^-	12.70	8.21	9.27	5.08	10.13
SeO_3^{2-}	3.70	3.78	6.18	2.83	2.97
$HAsO_4^{2-}$	4.60	4.65	7.13	3.78	3.48
SeO_4^{2-}	7.02	6.18	10.47	4.85	4.63
WO_4^{2-}	10.70	9.28	18.32	8.50	8.40
MoO_4^{2-}	14.37	12.11	21.62	10.15	11.55
GeO_3^{2-}	/	15.06	/	/	/
CrO_4^{2-}	28.89	22.45	29.28	12.87	23.97

* Flow-rate 0.9 mL min^{-1}

Phosphate eluent had low background absorption. But, when its concentration was high, it would also have high absorption. Thus, since the concentrations of the two eluents had big differences, although they had the same composition and pH value, all oxoanions could not be analyzed by a concentration gradient. Or else, some peaks would be swamped in high background absorption and difficult to be quantified.

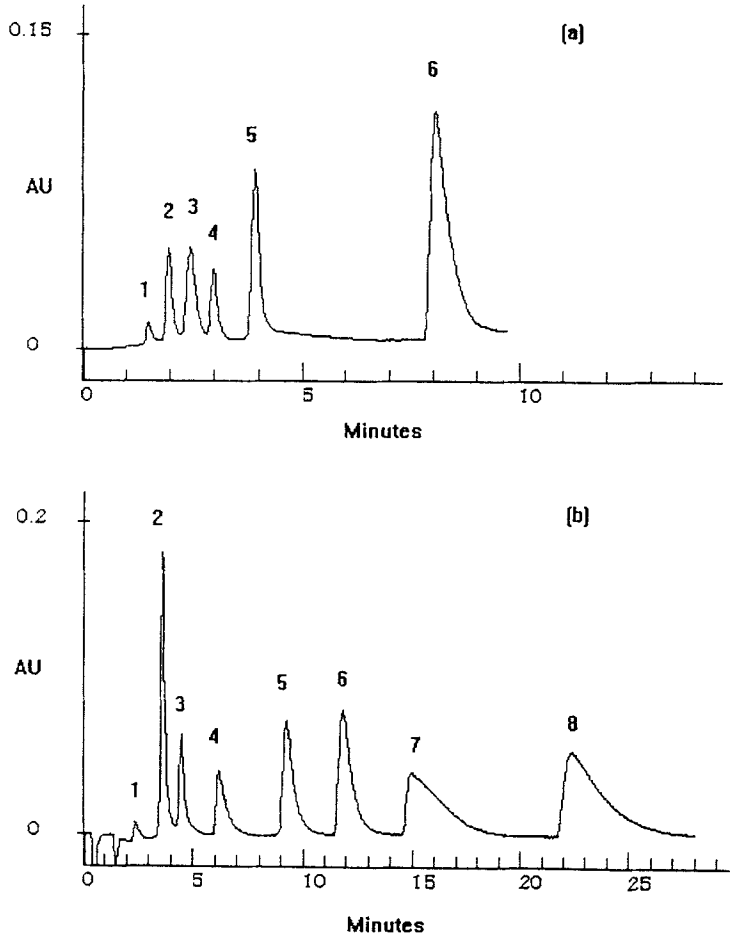

Figure 2. Chromatograms for the separation of oxoanions.

IonPac AS11 column had very low hydrophobicity. While using this column, the suitable eluents were 11 mM Na_2HPO_4, pH 9.3 for the analysis of SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, and CrO_4^{2-}, 0.5 mM Na_2HPO_4, pH 9.3 for the analysis of IO_3^-, $H_2AsO_3^-$, BrO_3^-, NO_2, and NO_3^-. As AS11 column also had low hydrophobicity and high hydrophilicity, the separations of most oxoanions had the same results as CS5A column. But, IO_3^- and $H_2AsO_3^-$ could not be separated by baseline (Rs=1.0). When the eluent concentration decreased, they may be well separated, but, the other oxoanions would be eluted for a long time and all their peaks would tail seriously.

IonPac AS4A-SC column has been usually used for the separation of oxoanions in the last decade.[4,6,7] It had medium-low hydrophobicity. While using this column, the suitable eluents were 3 mM Na_2HPO_4, pH 9.3 for the analysis of SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, and CrO_4^{2-}, 0.6 mM Na_2HPO_4, pH 9.3 for the analysis of IO_3^- / $H_2AsO_3^-$, BrO_3^-, NO_2^-, and NO_3^-.

IonPac AS9-SC analytical column had medium hydrophobicity. While using it, the suitable eluents were 10.5 mM Na_2HPO_4, pH 9.3 for the analysis of SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, and CrO_4^{2-}, 3.5 mM Na_2HPO_4, pH 9.3 for the analysis of IO_3^- / $H_2AsO_3^-$, BrO_3^-, NO_2^- and NO_3^-.

While using AS4A-SC and AS9-SC columns, the difference of elution time between IO_3^- and $H_2AsO_3^-$ was so small that they could not be separated. Whatever the eluent concentration and pH were, they could not be separated well. The other oxoanions could be separated, but, their separations were worse than that on the CS5A column.

IonPac PAX 500 column had reversed phase and /or anion exchange functional groups. Its anion functional groups had low hydrophobicity, however, its reversed phase groups had high hydrophobicity. This would result in poor separation.

While using the column, the suitable eluents were 4.5 mM Na_2HPO_4, 1% methanol, pH 9.3 for the analysis of SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, and CrO_4^{2-}, 0.2 mM Na_2HPO_4, 1% methanol, pH 9.3 for the analysis of IO_3^- / $H_2AsO_3^-$, BrO_3^-, NO_2^-, and NO_3^-. Among them, IO_3^-, $H_2AsO_3^-$, BrO_3^-, and NO_2^- could not be well separated and most peaks tailed seriously.

Furthermore, GeO_3^{2-} was eluted near to the dead time on the last four columns. When the eluent pH and concentration decreased, its peak tailed seriously and could not be quantified. But, it could be well separated on CS5A column and had a long elution time. This probably resulted in the special synergistic effect of the cation functional groups.

In general, it was seen that the hydrophilicity of the anion functional groups acted as an important role for the separation of oxoanions. The more hydrophilicity of the functional groups, the better separations of oxoanions. If there had other functional groups on the latex beads, high hydrophilicity of cation functional groups could improve their separation; high hydrophobicity of functional groups could make their separation worse.

Considering the detection limits, linear range, R.S.Ds, and resolution, the optimum analytical column order was CS5A > AS11 > AS4A-SC > AS9-SC > PAX 500. CS5A column was the best choice.

Choice of Eluent

The consideration for eluent selection was that all components must be non-absorbing in the desired wavelength range. For this reason, phosphate, citrate, and tartrate eluents were commonly used. Among them, phosphate eluent showed the lowest absorption at 204 nm while citrate and tartrate eluents exhibited higher absorption at this wavelength. Moreover, when citrate was used, some peaks showed up as inverted peaks and the WO_4^{2-} peak was absent. When tartrate was used, the NO_3^-, VO_3^{2-}, and MoO_4^{2-} peaks were overlapped. All these effects were undesirable. However, phosphate eluent gave no inverted peaks and all peaks were well separated. Thus, it was the best eluent for the analytical procedure.

Effect of Na_2HPO_4 Concentration

The Na_2HPO_4 concentration had a rather strong factor in its influence on the retention of oxoanions. Its effects on the selectivity were shown in Figs.3(a) and (b), respectively. The retention of all oxoanions, in general, became shorter with increasing eluent concentration. However, the differences in the retention time for different oxoanions were smaller at higher Na_2HPO_4 concentration. Thus, it was needed to make a compromise between selectivity and analytical time.

The ionic strength of the eluent increased with the eluent concentration and this would result in decreased interaction of anions with ion-exchange sites in the column. The retention of the oxoanions held strongly with ion-exchange sites had the same effect as that held loosely. It was shown clearly, by the fact that the capacity factor k' value of CrO_4^{2-} decreased from 21.72 to 7.82 (64.0% decrease), and that of SeO_3^{2-} from 2.15 to 0.77 (64.2% decrease) by increasing Na_2HPO_4 concentration from 6 mM to 15 mM, the capacity factor k' value of NO_3^- decreased from 4.74 to 3.64 (23.2% decrease) and that of IO_3^- from 0.39 to 0.29 (25.6% decrease) by increasing Na_2HPO_4 concentration from 0.45 mM to 1.2 mM. The other oxoanions had the same results.

When eluent concentration was higher than 10.5 mM / 0.9 mM, SeO_3^{2-} and $HAsO_4^{2-}$ / IO_3^- and $H_2AsO_3^-$ could not be separated by baseline, respectively. When eluent concentration was lower than 7.5 mM / 0.9 mM, the retention of these oxoanions became greater and consequently the peaks would broaden seriously. Based on a consideration of the above factors, 7.5 mM Na_2HPO_4 eluent was chosen to analyze SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, GeO_3^{2-}, and CrO_4^{2-}; 0.75 mM Na_2HPO_4 was chosen to analyze IO_3^-, $H_2AsO_3^-$, BrO_3^-, NO_2^-, and NO_3^-.

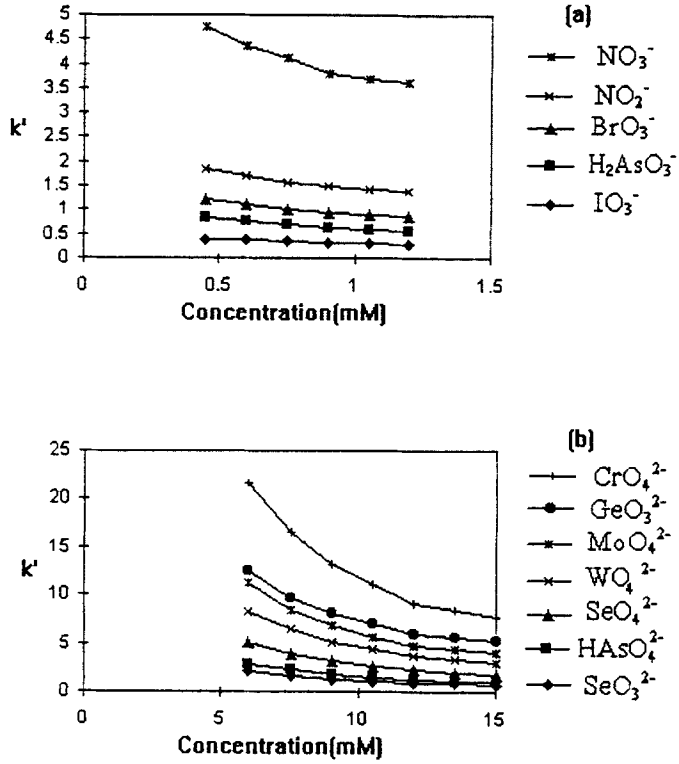

Figure 3. The effects of Na_2HPO_4 concentration on the capacity factor (k') for oxoanions.

Effect of Methanol Concentration

Sometimes, organic modifiers had special roles for separation. They could modify the shapes of peaks and selectivities of separation. In this paper, methanol was tested as the organic modifier. The retention of oxoanions in general became shorter with increasing methanol concentration.

The variabilities of all oxoanions were not obvious, they had only a little change. The shapes of peaks and selectivities of separation were not improved. Because their separations were based on ion exchange, organic modifiers had no effect on the separation. Thus, organic modifiers were not needed.

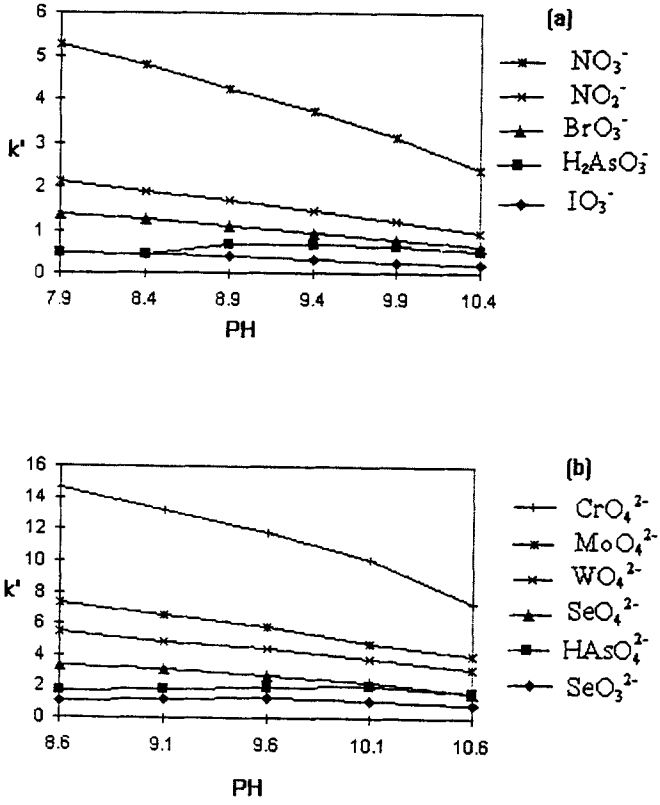

Figure 4. The effects of pH on the capacity factor (k') for oxoanions.

Effect of pH

The pH of the eluent had a strong effect on the retention and shape of the analyte peaks (shown in Fig.4). Their retentions were a function of the pH value. The pH could affect the ionic charge on multicharge phosphate anion (PK_2=7.2 and PK_3=12.3). The ionic charge and eluent strength was greater at higher pH of the eluent, which led to shorter elution time. On the other hand, the pH could also affect the valence states of multicharge oxoanions. Their valence states were greater at higher pH of the eluent. The percent of high valence oxoanions would increase. This led to longer elution time. It was seen from Fig.4 that the elution time of SeO_3^{2-}, $HAsO_4^{2-}$, and $H_2AsO_3^-$ increased first, and then decreased with the increasing pH. The elution time of the other oxoanions only decreased.

Table 3

Linear Ranges, Correlation Coefficients, R.S.Ds. and Detection Limits of Oxoanions

Oxoanion	Concentration Range ($\mu g\ mL^{-1}$)	Correlation Coefficient (r)[1]	R.S.D. (%)[2]	Detection Limit[3] ($\mu g\ mL^{-1}$)
IO_3^-	0.3 - 40	0.9998	0.9	0.04
$H_2AsO_3^-$	0.15 - 20	0.9992	1.4	0.03
BrO_3^-	0.3 - 40	0.9996	2.0	0.06
NO_2^-	0.08 - 20	0.9999	2.6	0.02
NO_3^-	0.15 - 20	0.9990	1.5	0.03
SeO_3^{2-}	0.2 - 200	0.9991	2.3	0.05
$HAsO_4^{2-}$	0.2 - 40	0.9995	2.0	0.5
SeO_4^{2-}	1.6 - 200	0.9993	1.7	1.0
WO_3^{2-}	0.6 - 80	0.9997	1.9	0.2
MoO_4^{2-}	0.3 - 40	0.9999	1.7	0.1
GeO_3^{2-}	5 - 80	0.9991	1.7	1.1
CrO_4^{2-}	1 - 40	0.9998	1.6	0.3

[1] diluted 1:1, 1:2, 1:4, 1:8, 1:16, 1:32, 1:64, 1:128
[2] concentration > 10X detection limits (n=7)
[3] Signal-to-noise 3:1

When the pH > 10.1, $HAsO_4^{2-}$ could not be well separated with SeO_4^{2-}. When the pH < 8.9, IO_3^- could not be well separated with $H_2AsO_3^-$. From Fig.4, pH 9.3 was selected as the best.

Under the optimized conditions, the chromatograms for the separation of different oxoanions were shown in Fig.2. It was seen that the different oxidations of N, As and Se were well separated.

Accuracy and Detection Limits

The working linear ranges, detection limits, correlation coefficients, and R.S.Ds. for various oxoanions were shown in Table 3. All oxoanions had good linearities, whose correlation coefficients were greater than 0.999. The R.S.Ds. based on >10X detection limits concentration were found to be in the range of 0.9% - 2.6% and the detection limits (signal-to-noise ratio 3:1) of this method were at or below ppm level.

CONCLUSIONS

This paper provided a developed analytical procedure, which was capable of multi-oxoanions determination. Since the presence of chloride, fluoride, sulfate, and perchlorate did not absorb at 204 nm, they did not interfere with the analysis. This was an advantage of using direct UV absorption detection, but, the detection limits were not low enough for some environmental samples.

If this method was coupled with other detection techniques, such as atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled argon plasma emission spectrometry (ICP), inductively coupled plasma mass spectrometry (ICP-MS), and post-column derivatization for metalloids, electrochemical detector for SeO_3^{2-} and $H_2AsO_3^-$, it would be an attractive analytical method for element and element speciations.

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