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## SEPARATION OF OXOANIONS BY ION CHROMATOGRAPHY USING ANION- EXCHANGE RESIN HIKS-1

Priit ALUMAA and Jaan PENTSUK

Tartu Ülikooli Keemilise Füüsika Instituut (Institute of Chemical Physics, Tartu University), Jakobi 2, EE-2400 Tartu, Eesti (Estonia)

Presented by U. Kirso

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OKSOANIOONIDE IOONKROMATOGRAAFILINE LAHUTAMINE SORBENDIGA  
HIKS-1. Priit ALUMAA, Jaan PENTSUK

РАЗДЕЛЕНИЕ ОКСОАНИОНОВ МЕТОДОМ ИОННОЙ ХРОМАТОГРАФИИ С  
СОРБЕНТОМ ХИКС-1. Прийт АЛУМАА, Яан ПЕНЧУК

**Key words:** ion chromatography, oxoanions, optimization.

The purpose of the present work was to find the optimal conditions for the simultaneous suppressed anion-chromatographic determination of such oxoanions as sulphate, selenate, and arsenate, and metals of the chromium group on the low-capacity resin HIKS-1.

The relationship between the adjusted retention time of oxoanions and the concentration and pH of the  $\text{Na}_2\text{CO}_3 + \text{NaOH}$  eluent was studied.

### EXPERIMENTAL

**Instrumentation.** An EAK (Design Office of the Estonian Academy of Sciences) model IVK-21 ion chromatograph with a model JD-1 conductivity detector and КСП-4 recorder was used. Anion separator columns of  $150 \times 3$  mm and  $250 \times 3$  mm were packed with the anion-exchange resin HIKS-1 (25—40  $\mu\text{m}$ ). Suppressor column of  $250 \times 4$  mm was packed with the cation-exchange resin KU-2. The injection loop was 100  $\mu\text{l}$  and the eluent flow rate, 1.0—1.2 ml/min.

**Reagents and procedures.** All the reagents used (Reakhim) were of analytical grade. The eluents were prepared by dissolving preheated  $\text{Na}_2\text{CO}_3$  in bidistilled water and adding NaOH to adjust the pH value. Standard solutions of anions were prepared from stock solutions (400—1000 mg/l) of the potassium and sodium salts.

## RESULTS AND DISCUSSION

Oxoanions of the chromium group of elements (tungsten, molybdenum, chromium) are strongly retained in the anion separator column, so the standard eluent (2.4 mM  $\text{CO}_3^{2-}$ +3.0 mM  $\text{HCO}_3^-$ ) gives long retention times and poor sensitivity [1-3]. Thus, for rapid determination an eluent with greater eluting strength is needed. On the other hand, the selenate, sulphate and at some pH values [4] also arsenate ion retention times compared with those of the chromium group are relatively small. For this reason there are certain difficulties in simultaneous determination of the above-named oxoanions.

The results obtained with the 150×3 mm separator column (Table 1) show that the separation of anions is insufficient for their simultaneous determination due to the very low resolution of arsenate/sulphate and sulphate/selenate ions. The changing of the eluent concentration gave no better resolving effect for those two ion pairs.

Table 1

The effect of the  $\text{Na}_2\text{CO}_3$  concentration ( $C$ , mM) in the eluent on the separation factor<sup>1</sup> ( $\alpha$ ) of oxoanions with separation columns 150×3 mm (A) and 250×3 mm (B)

C, mM	$\alpha$									
	$\text{SO}_4^{2-}/\text{AsO}_4^{3-}$		$\text{SeO}_4^{2-}/\text{SO}_4^{2-}$		$\text{WO}_4^{2-}/\text{SeO}_4^{2-}$		$\text{MoO}_4^{2-}/\text{WO}_4^{2-}$		$\text{CrO}_4^{2-}/\text{MoO}_4^{2-}$	
	A	B	A	B	A	B	A	B	A	B
2.0	1.08	1.06	1.11	1.22	1.38	—	1.21	—	1.31	—
2.4	1.09	1.08	1.20	1.21	1.28	1.21	1.20	1.30	1.44	1.59
3.0	1.06	1.09	1.11	1.18	1.24	1.25	1.33	1.25	1.46	1.62
3.5	—	1.09	—	1.16	—	1.19	—	1.26	—	1.68
4.0	1.06	—	1.13	—	1.14	—	1.46	—	1.55	—

<sup>1</sup> The ratio of adjusted retention times for the two solutes between which the resolution is being calculated.

Table 2

Adjusted retention time ( $t'$ , min) and column efficiency<sup>1</sup> (HETP, mm) values for oxoanions. Eluent: 3.0 mM  $\text{Na}_2\text{CO}_3$

Anion	Column			
	150×3 mm		250×3 mm	
	$t'$	HETP	$t'$	HETP
arsenate	1.80	2.53	4.65	1.68
sulphate	1.90	1.88	5.10	0.98
selenate	2.10	2.21	6.00	1.01
tungstate	2.60	2.56	7.50	1.81
molybdate	3.45	8.16	9.30	3.01
chromate	5.05	1.53	15.00	1.02

<sup>1</sup>  $\text{HETP} = L/5.54(t'/\tau)^2$ , where  $L$  is the column length,  $t'$  is the adjusted retention time and  $\tau$  is the peak width measured at half height.

To enhance the separation efficiency a separation column of greater length was used (see Table 2). The effect of the eluent concentration on the adjusted retention time for anions on using the 250×3 mm column is shown in Figure 1. The plots are straight lines with almost similar slopes in the range of 0.91 to 1.08.

As one can see from the data in Table 1, it is necessary to use low  $\text{CO}_3^{2-}$  concentrations to achieve an acceptable resolving of sulphate/selenate. Unfortunately this increases the analysis time due to the long retention time of molybdate and chromate. The separation of arsenate/sulphate is insufficient even at eluent concentrations lower than 2.0 mM  $\text{Na}_2\text{CO}_3$  (see Fig. 1).

The effect of the eluent pH on the adjusted retention time for anions was studied by plotting the logarithm of the adjusted retention time versus NaOH concentration in the eluent (Fig. 2). The sodium carbonate concentration used was 2.0 mM. The results showed that retention times shortened when the eluent pH increased with the exception of the arsenate ion. The increase in the arsenate ion retention time is due to the increase in its negative charge at higher pH values.

The best resolution of the oxoanions studied was achieved at the NaOH concentration of 2.7 mM (Fig. 2). In this case the arsenate peak was situated exactly between the chromate and molybdate peaks (Fig. 3).

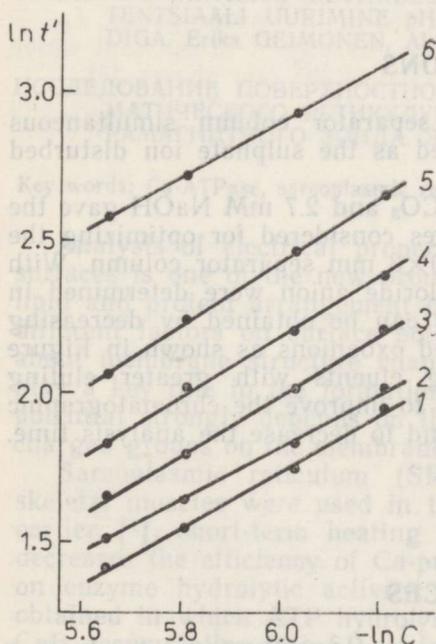


Fig. 1. Adjusted retention time ( $\ln t'$ ) vs. eluent concentration ( $-\ln C$ ) plots for oxoanions using  $\text{Na}_2\text{CO}_3$  eluents and 250×3 mm separator column. 1 — arsenate, 2 — sulphate, 3 — selenate, 4 — tungstate, 5 — molybdate, 6 — chromate.

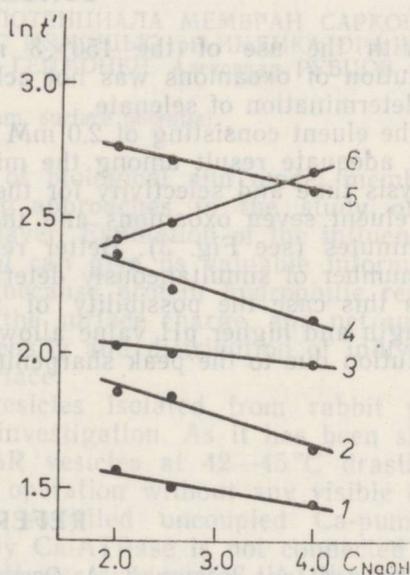


Fig. 2. Adjusted retention time ( $\ln t'$ ) vs. NaOH concentration in the eluent ( $C_{\text{NaOH}}$ ) plots for oxoanions using 2.0 mM  $\text{Na}_2\text{CO}_3 + X$  mM NaOH eluents and 250×3 mm separator column. 1 — sulphate, 2 — selenate, 3 — tungstate, 4 — molybdate, 5 — chromate, 6 — arsenate.

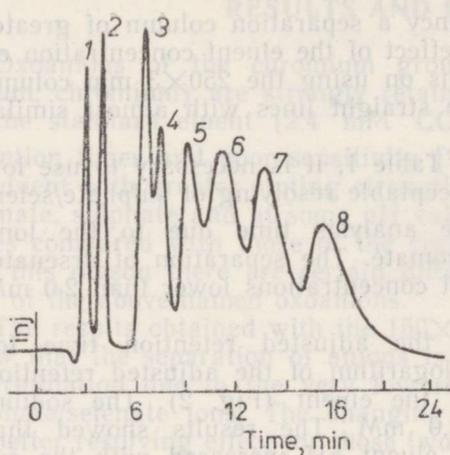


Fig. 3. Optimized chromatogram for the simultaneous separation of oxoanions. Conditions: separator column 250×3 mm, eluent 2.0 mM Na<sub>2</sub>CO<sub>3</sub>+2.7 mM NaOH, solute concentrations 5–70 ppm. Ions: 1 — chloride, 2 — nitrate, 3 — sulphate, 4 — selenate, 5 — tungstate, 6 — molybdate, 7 — arsenate, 8 — chromate.

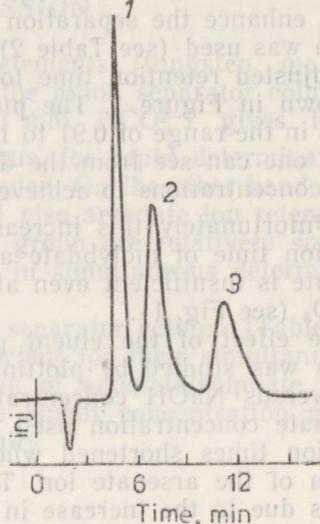


Fig. 4. Separation of oxoanions. Conditions: separator column 250×3 mm, eluent 2.4 mM Na<sub>2</sub>CO<sub>3</sub>+5.0 mM NaOH. Ions: 1 — sulphate (10 ppm), 2 — tungstate (70 ppm), 3 — arsenate (30 ppm).

## CONCLUSIONS

With the use of the 150×3 mm separator column simultaneous resolution of oxoanions was not achieved as the sulphate ion disturbed the determination of selenate.

The eluent consisting of 2.0 mM Na<sub>2</sub>CO<sub>3</sub> and 2.7 mM NaOH gave the most adequate result among the mixtures considered for optimizing the analysis time and selectivity for the 250×3 mm separator column. With this eluent seven oxoanions and the chloride anion were determined in 20 minutes (see Fig. 3). Better results can be obtained by decreasing the number of simultaneously determined oxoanions as shown in Figure 4. In this case the possibility of using eluents with greater eluting strength and higher pH value allows us to improve the chromatographic resolution due to the peak sharpening and to decrease the analysis time.

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