ISSN 0027-1314, Moscow University Chemistry Bulletin, 2008, Vol. 63, No. 6, pp. 333–337. © Allerton Press, Inc., 2008.
Original Russian Text © T.I. Tikhomirova, N.M. Sorokina, O.O. Lashtabega, D.N. Konshina, V.V. Konshin, Z.A. Temerdashev, G.I. Tsizin, 2008, published in Vestnik Moskovskogo Universiteta. Khimiya, 2008, No. 6, pp. 403–408.

Preconcentration of Anionic Forms of Chemical Elements on Filters with Anchored Quaternary Ammonium Groups

T. I. Tikhomirova, N. M. Sorokina, O. O. Lashtabega[a], D. N. Konshina[a], V. V. Konshin[a], Z. A. Temerdashev[a], and G. I. Tsizin
Department of Analytical Chemistry
e-mail: tsisin@analyt.chem.msu.ru

Received December 20, 2007

Abstract—Sorption of silicomolybdic acid (SMA) and phosphovanadomolybdic acid (PVMA) and arsenic(V), vanadium(V), and chromium(VI) anionic species is studied on cellulose filters with bound quaternary ammonium groups. These heteropoly acids (HPAs) are recovered in quantity on filters from solutions with high salt backgrounds and with high mineral acid concentrations. AsO_4^{3-}, CrO_4^{2-}, and VO_3^- anions are sorbed at pH of 3–9. In this case, the ionic strength considerably influences anion recovery. Conditions were found for preconcentrating vanadium, arsenic, and chromium from 250-mL aliquots of aqueous solutions (the preconcentration coefficient was 5×10^3). A procedure was proposed for the sorption/X-ray fluorescence determination of these elements in high-purity water.

DOI: 10.3103/S0027131408060060

Cellulose filters with anchored functionalities are used for preconcentrating inorganic ions from solutions. For the subsequent determination of chemical elements, these filters are usually burnt of dissolved [1]; however, X-ray fluorescence determination directly on the filter is more promising [2]. This approach combines advantages of both preconcentration and subsequent determination. Filters, being a light matrix, provide for high preconcentration coefficients, the unified compositions and weights of radiator samples, and an increased sensitivity of X-ray fluorescence determination of chemical elements.

Filters with anchored complexing groups are used more frequently [3]; filters bearing ionic groups, such as secondary and tertiary amino groups [4], are used less frequently because of the moderate efficiency and salt background dependence of preconcentration. Quaternary ammonium groups have a higher basicity than secondary or tertiary amino groups [5]; therefore, filters modified with quaternary ammonium groups should be more efficient for preconcentrating anions.

This work studies the recovery of molybdic heteropoly acids (HPAs) of silicon and phosphorus, as well as arsenic(V), vanadium(V), and chromium(VI) anionic species, on cellulose filters containing tetraalkylammonium chloride and tetraalkylammonium iodide groups.

EXPERIMENTAL

Reagents and equipment. Solutions (1×10^{-3} mol/L) of phosphovanadomolybdic acid (PVMA) $H_4[PVMo_{11}O_{40}] \cdot 20H_2O$ and silicomolybdic acid (SMA) $H_4[SiMo_{12}O_{40}] \cdot 13H_2O$ were prepared by dissolving weighed samples of acids in distilled water. The stock arsenic solution (1 mg/mL) was prepared by dissolving a weighed Na_3AsO_4 sample (chemically pure grade) in distilled water. Working solutions of arsenic(V) were prepared by diluting the stock solution; those of chromium(VI) and vanadium(V) were prepared by diluting standard solution samples (1 mg/mL) purchased from Ecoanalytica.

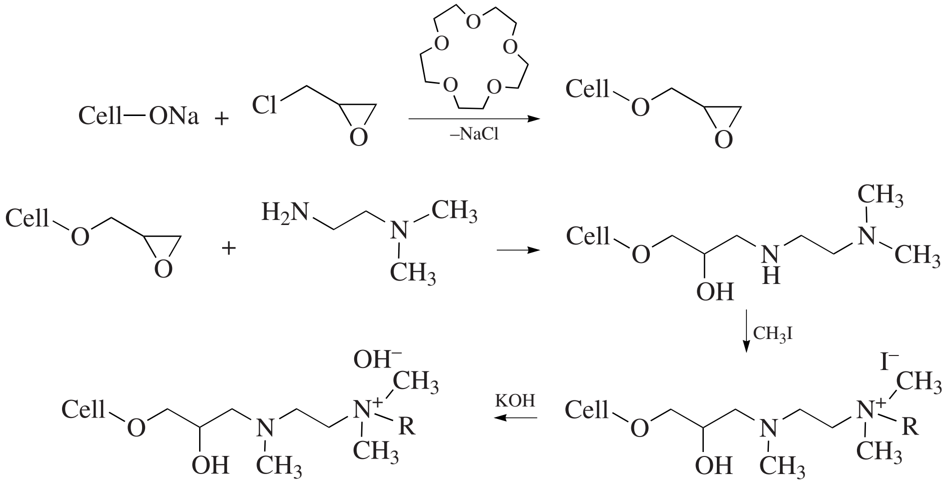
1 M Na_2SO_4 and 2 M NaCl solutions were prepared by dissolving weighed samples of the salts in distilled water. 5 M sulfuric acid was prepared by diluting concentrated acid; 5% ascorbic acid solution was prepared by dissolving a weighed sample in water.

pH was adjusted using 0.1 M NaOH and HCl.

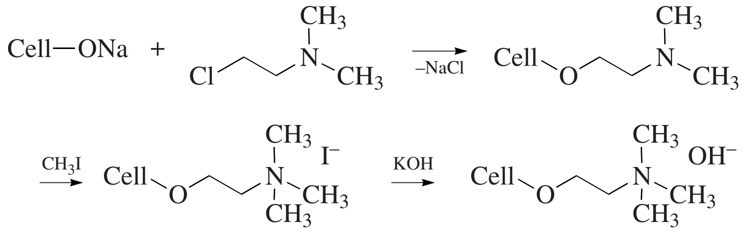
Celluloses filters containing tetraalkylammonium iodide groups were prepared by Schemes 1 and 2. Filters were designed using paper filters of various densities (Table 1). In addition, anion recovery was studied on cellulose filters with anchored diethylenetriamine groups, as proposed by Smits and van Grieken [6]. Ions were sorbed on filters mounted in holder cells (Millipore). The solution was passed through a cell with the use of a Ros-Analyt peristaltic pump. Acidity was monitored with a pH meter model 121. Diffuse reflectance

---

[a] *Department of Analytical Chemistry, Faculty of Chemistry, Kuban State University*



Scheme 1.



Scheme 2.

spectra were measured on a Spectroton (Khimavtomatika) photocolorimeter.

Vanadium, arsenic, and chromium were determined on filters using a Spectroscan-U (Spectron) portable X-ray fluorescence spectrometer equipped with a molybdenum anode and an LiF200 analyzer crystal with the supply voltage 40 kV and current 0.5 mA. Silicon and phosphorus were determined on a Spectroscan-GV (Spectron) vacuum wavelength-dispersive scanning X-ray fluorescence spectrometer.

Procedures. To study the sorption of silicon and phosphorus HPAs, an HPA solution was placed into a 25-mL flask; then, sodium antimonyl tartrate (0.1 mL) and ascorbic acid solutions were added. In studying the influence of the ionic strength and acidity on HPA recovery, the appropriate salt solutions and sulfuric acid were added to a flask, and distilled water was added to bring the aqueous phase volume to 25 mL. The resulting solution was passed through a filter at 5 mL/min. The filters were dried in air, and the diffuse reflectance at $\lambda = 720$ nm or X-ray fluorescence intensity was measured.

In studying the sorption of arsenic, chromium, and vanadium anionic species, the recovery completion was monitored by measuring the X-ray fluorescence intensity on the filter after the passage of the solution containing all elements. The percentages of the chemical elements on the filter was determined from the calibration plot plotted using references, which were prepared by dropping solutions of known concentrations on filters.

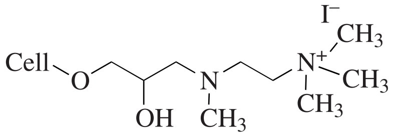
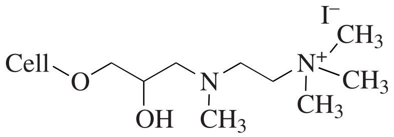
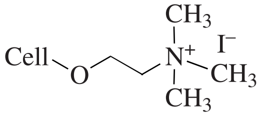
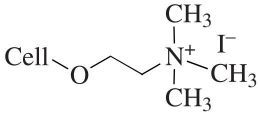
RESULTS AND DISCUSSION

On filters with anchored quaternary ammonium groups, sorption mostly occurs via ion exchange; therefore, competition between anions is possible. With changing solution acidity, recovery can be influenced by the following two factors: competition from mineral acid anions and a change in the ionic state of the recovered anionic species (protonation); for HPAs, the decay of hetero complexes comes is also in play. To choose optimal conditions, we studied recovery as a function of ionic strength and mineral acid concentration.

Sorption of reduced species of silicon and phosphorus HPAs. Reduced species of silicon and phosphorus HPAs are intensely colored blue; therefore, diffuse reflectance spectroscopy is a pertinent tool for controlling HPA recovery via measuring diffuse reflectivity R at 720 nm. Function F was calculated from

$$F = (1 - R)^2/2R.$$

Table 1. Filters used for preconcentrating anionic species of chemical elements

Type	Structure	Paper density, g/m^2	Capacity, mmol/(L g)
I		140	0.7 ± 0.05
II		100	0.6 ± 0.06
III		100	0.44 ± 0.05
IV		160	0.38 ± 0.02
V		140	2.4 ± 0.2*

* Nitrogen capacity.

Table 2 lists the values of function F for HPA recovery on filters (type I) from solutions with various sodium chloride concentrations. These values make it clear that SMA and PVMA sorption is almost unaffected by sodium chloride percentage within 0–1.8 mol/L. In the presence of doubly charged sulfate ions, PVMA sorption insignificantly decreases, whereas SMA recovery remains unchanged.

SMA and PVMA sorption does not change while sulfuric acid percentages are 0–1.5 and 0–0.5 mol/L, respectively (Table 3). The decrease in HPA recovery with increasing sulfuric acid percentage is due to the protonation-induced decrease in the charge of the heteropoly anion. Possible is also partial degradation of heteropoly complexes; this is more significant for sorption of less strongly bonded phosphorus complexes. Our study provided for choosing parameters for joint preconcentration of molybdenum HPAs of silicon and phosphorus on filters with anchored quaternary ammonium groups from aqueous solutions, including solutions with high salt backgrounds, for the further X-ray fluorescence determination of these elements. The X-ray fluorescence signal intensity is a linear function of HPA percentage in the solution for recovering silicon and phosphorus from a 25-mL solution aliquot containing 5×10^{-6} to 1×10^{-4} mol/L of these elements.

Recovery of arsenic(V), chromium(VI), and vanadium(V) anionic species. The sorption of arsenic(V), chromium(VI), and vanadium(V) anionic species was studied on filters I, which contain quaternary ammonium chloride and iodide groups. The recovery of anions is almost not influenced by the counterion (whether it is chloride or iodide) in the tetraalkylammonium group, but is influenced by the charge density of the anion to be recovered.

Table 2. Function F for SMA and PVMA recovery as a function of sodium chloride and sodium sulfate concentration ($c_{\text{SMA}} = 3 \times 10^{-5}$ mol/L; $c_{\text{PVMA}} = 4 \times 10^{-5}$ mol/L; $V_{\text{aq}} = 25$ mL)

c_{NaCl}, mol/L	F_{SMA}	F_{PVMA}	$c_{\text{Na}_2\text{SO}_4}$, mol/L	F_{SMA}	F_{PVMA}
0	2.7	3.8	0	2.4	3.8
0.3	2.9	3.9	0.2	2.5	2.5
0.7	2.7	3.6	0.4	2.5	2.5
0.6	3.0	3.5	0.8	2.4	1.6
1.8	2.8	3.6	–	–	–

Table 3. Function F for SMA and PVMA recovery as a function of sulfuric acid concentration ($c_{\text{SMA}} = c_{\text{PVMA}} = 4 \times 10^{-5}$ mol/L; $V_{\text{aq}} = 25$ mL)

$c_{\text{Na}_2\text{SO}_4}$, mol/L	F_{SMA}	F_{PVMA}
0	4.8	3.9
0.5	4.9	3.8
1.0	4.8	2.0
1.5	5.0	1.5
2.0	3.7	0.7

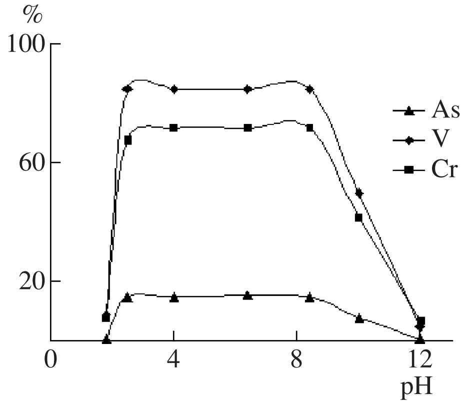


Fig. 1. Arsenic(V), vanadium(V), and chromium(VI) recovery on filters vs. aqueous pH. $V_{aq} = 25$ mL; $c_{el} = 50$ μg; $v = 4$ mL/min.

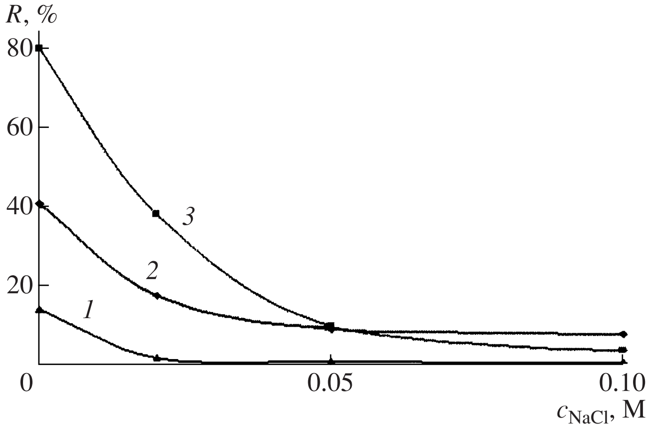


Fig. 2. (*1*) Arsenic(V), (*2*) vanadium(V), and (*3*) chromium(V) recovery on filters vs. solution ionic strength. $c_{el} = 50$ μg; $v = 4$ mL/min; $V_{aq} = 30$ mL; pH 3.2.

The data in Fig. 1 show that sorption decreases in the following order: chromate > vanadate > arsenate. The maximal recovery for all elements is within pH 3–8. The reduction in sorption at pH > 8 is related to the competition from hydroxide ions; at pH < 3, it is because of the protonation of anionic species and the competition from mineral acid anions. A change in the flow rate of the analyte sample within 4–10 mL/min does not influence the recovery of chromium and arsenic anionic species; at higher solution flow rates, however, the vanadium recovery decreases. Therefore, in further experiments, the flow rate did not exceed 4 mL/min. For arsenic, vanadium, and chromium anionic species, unlike for HPAs, increasing ionic strength considerably influences the recovery. The recovery is halved with increasing sodium chloride concentration to 0.02 mol/L (Fig. 2).

Table 4. Percent recovery (%) of anionic species of chemical elements on various types of filters (pH 4.5; $V_{aq} = 30$ mL; $c_{el} = 50$ μg)

Type	Recovery, %				
Element	I	II	III	IV	V
As	17	24	10	22	40
Cr	96	38	21	31	38
V	70	34	16	22	27

Table 5. Arsenic (V), chromium (VI), and vanadium (V) determination in distilled water ($V = 100$ mL; pH 5.8; $n = 3$; $P = 0.95$)

Element	Added, μg	Found, μg
As	0	0
	10	9.9 ± 2.2
	20	18.0 ± 2.5
Cr	0	1.0 ± 0.2
	10	10.3 ± 0.7
	20	19.5 ± 2.3
V	0	2 ± 0.3
	10	11 ± 1
	20	19 ± 3

We studied the recovery of arsenic, vanadium, and chromium anionic species on filters of various capacities, as well as on filters having various structures and basicities of anion-exchange groups. The results are compiled in Table 4. The recovery on type I filters is more efficient than on type II, III, and IV filters, which may be explained by a higher capacity of type I filters. Sorption on filters containing DETA groups is less efficient, despite their greater capacities compared to type I filters.

Samples for plotting calibration curves for X-ray fluorescence determination were prepared by sorption on type I filters. The linear region of the calibration curve was 0–20 μg for arsenic and 0–50 μg for chromium and vanadium for recovery from 30-mL solution aliquots. For the chemical elements studied, the recovery did not change when the aliquot volume changed to 250 mL; the maximal preconcentration coefficient was 5×10^3. The detection limits for arsenic, chromium, and vanadium on filters calculated using the 3*s* test were 0.6, 0.9, and 1.6 μg, respectively.

Distilled water was analyzed under optimal recovery conditions (Table 5). The adequacy of arsenic, chromium, and vanadium determinations was validated by the added/found method.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 06-03-96655-r_yug_a and 06-03-32178-a).

REFERENCES

1. Hata, N., Yamada, H., Kamada, I., and Taguchi, S., *Analyst*, 1999, vol. 124, p. 23.
2. Lio Ping, Kazuko Matsumoto, and Keiichiro Fuwa, *Anal. Chem.*, 1983, vol. 55, p. 1819.
3. Gennaro, M.C., Mentasti, E., and Sarzanini, C., *New J. Chem.*, 1986, vol. 10, p. 107.
4. Kulagina, N.V., Tikhomirova, T.I., Sorokina, N.M., Fadeeva, V.I., Tsizin, G.I., and Zolotov, Yu.A., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1993, vol. 35, p. 167.
5. Shmidt, V.S., *Ekstraktsiya aminami* (Extraction by Amines), Moscow, 1980.
6. Smits, J. and van Grieken, R., *Anal. Chim. Acta*, 1981, vol. 123, p. 9.