Sorbents for the Removal of Organic Compounds that Interfere with the Determination of Bromide in Natural Waters**

Yu.I. Mazna, O.V. Zuy*

Dumansky Institute of Colloid and Water Chemistry of the National Academy of Sciences of Ukraine, 42 Vernadsky blvd, Kyiv, Ukraine, 03142; *e-mail: olegzuy@gmail.com

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A number of porous polymeric solid phase extracting sorbents were tested for selective removal of organic compounds from aqueous solutions in which bromide ions are to be determined, and the best were recommended. A methodology was developed to achieve selectivity as to bromide ion, the concentration of which should not change in the sample during sample pretreatment. In order to selectively remove dissolved organic compounds from water matrix intended for analysis for bromide, sample acidification to pH 2.0 is recommended followed by sample filtration through the reverse-phase sorbent of LC-18 type. In these conditions, 20 mg/dm^3 of fulvic acid characteristic of Dnipro River water are effectively separated from 0.1 mg/dm^3 Br$^-$ with minimal losses of the latter. Sample acidification promotes the formation of molecular non-dissociated forms of organic compounds in solution, which are effectively separated from bromide ions on reverse-phase sorbents. Artesian water and sea water contaminated with oil spills were analyzed using passing through LC-18 sorbent. Results of natural water analysis by photometric and ICP-MS methods prove the applicability of the approach proposed.

Keywords: porous polymeric sorbents; selective organics removal; sample pretreatment; pH optimization

Bromide ions are a source of carcinogenic bromate ions in drinking water treated with ozone or other oxidizing disinfectants [1]. Various time-consuming methods are used to remove bromates from water, most of which are based on sorption of bromate ions [2-5]. It is known that the threshold concentration of bromides at which significant amounts of bromates are formed during water disinfection, is 0.04-0.05 mg/dm^3 [6]. Therefore, bromides should be monitored with appropriate sensitivity in waters of different types to prevent bromates formation at the level of their maximum allowable concentration (10 μg/dm^3) and above it.

Photometric and ion chromatographic methods are the most common ones in the analysis of water for bromides [7]. In these methods, an interfering effect of dissolved organic compounds present in water is observed [8, 9]. This interfering effect in the case of photometric methods of analysis is associated with a competitive bromination reaction on the aromatic rings of these organic compounds, which does not give a blue product similar in color to the dye Bromophenol Blue - the bromination product of the dye Phenol Red which is used in the standard photometric method for bromide [10]. In ion chromatography, organic compounds also affect the retention of bromide ions. To obtain reliable, correct results of analysis, dissolved organic compounds must be selectively removed from the solution so that the concentration of bromide in it does not change.

Separation of bromide from aqueous matrix containing natural organic matter was described using AgCl – activated carbon composite [11], utilizing formation of unsoluble AgBr, however, this method is aimed on reduction of brominated organics formation during water disinfection and not on subsequent bromide determination.

Removal of natural organic matter during drinking water production was described by using ion exchange, microfiltration with in-line coagulation followed by granular activated carbon filtration [12], but significant amounts of bromide were also removed from solution during such treatment. Another approach was proposed based on gas extraction of volatile bromine from aqueous solution by the flow of purified air [13, 14]. Volatile bromine was trapped by aqueous solution and thus separated from organic and other components present in the sample. Acidified potassium dichromate solution was used as an oxidant for bromide oxidation to bromine. Dilute bromine in aqueous solution decomposes instantly with formation of bromide and oxygen. Organic substances – humic and fulvic acids – are decomposed in presence of acidified dichromate with formation of non-volatile products. The drawback of such approach is the use of toxic potassium dichromate in the procedure.

In this study, a number of sorbents were examined for selective removal of dissolved organic matter and their suitability was checked for subsequent bromide determination in water.

Materials and methods

Equipment and reagents

Spectra in the ultraviolet and visible regions were recorded on a Shimadzu 2450 spectrophotometer. The pH was measured with an ionometer EV-74 with a glass electrode. The Agilent 7500 ce ICP-MS spectrometer was used to obtain total bromine concentrations. Distilled water obtained in a glassy distillation apparatus was used throughout. Fulvic acid (isolated from the Dnipro River water) was used as a model organic compound to study the effect and removal of interfering with the determination of bromide ions organic substances, given that solutions of fulvic acids in the ultraviolet region exhibit a higher optical density than solutions of humic acids of the same mass concentration. Humic acid was purchased from Sigma-Aldrich. Bromide solutions were prepared from KBr salt of analytical grade. For samples acidification sulfuric acid of analytical grade was used.

Dissolved organic compounds sorption studies

The spectra of fulvic acid were recorded before and after passing through sorbents of various types, including through columns for solid-phase extraction Supelclean LC-18, Supelclean LC-8, SAX, Alumina-N, Amberlite XAD-2, DEAE-cellulose, Polysorb-1, Silasorb SPH C18, Silasorb SPH C8, Supelclean ENVI-18. The columns were preconditioned first with 2 cm^3 of 96% ethanol, then washed with 2 cm^3 of water. From 2 to 10 cm^3 of the sample was passed through a column, the first 10 drops of filtrate were discarded. The remaining filtrate was used to record the absorption spectra of organic substances in ultraviolet region or to perform a photometric reaction for bromide ions.

Results and discussion

Selection of the sorbents

For selective organics removal ion-exchange and reverse-phase sorbents were tested. In order to reveal light absorbance of some water components in UV-region spectra in the range 200-400 nm of solutions at neutral and acidic pH were recorded: distilled water, fulvic acids, humic acids, nitrate ions, bicarbonate ions, bromide ions. Spectra of neutral model solutions are shown on Fig. 1, spectra of solutions acidified to pH 2.0 – on Fig. 2.

Figures 1 and 2 show that solutions of humic acids, both acidified and not acidified, in the ultraviolet have a much lower optical density than solutions of fulvic acids of the same mass concentration.

Spectra of fulvic acid solutions in UV region were recorded before and after passing through Supelclean ENVI-18, SAX, Strata SDB-L, LC Alumina-N, XAD-2, Polysorb-1 cartridges. These spectra are shown in Figures 3 and 4.

It can be seen from Figures 3 and 4 that fulvic acid is effectively removed from aqueous solutions by the SAX cartridge having the volume of 3 cm^3.

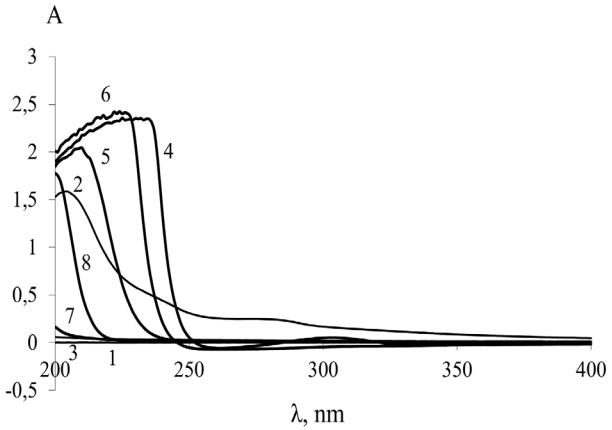

Fig. 1. Spectra of neutral solutions: distilled water (1), fulvic acid 20 mg/dm^3 (2), humic acid 20 mg/dm^3 (3), nitrate ions 1000 mg/dm^3 (4), nitrate ions 20 mg/dm^3 (5), nitrate ions 200 mg/dm^3 (6), bicarbonate ions 200 mg/dm^3 (7), bromide ions 20 mg/dm^3 (8).

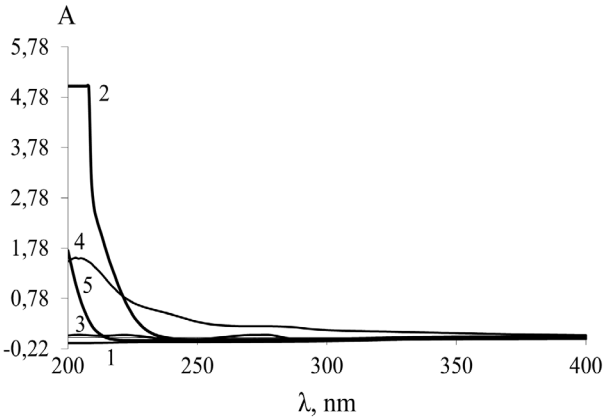

Fig. 2. Spectra of solutions acidified with sulfuric acid to pH 2.0: distilled water (1), nitrate ions 20 mg/dm^3 (2), humic acid 20 mg/dm^3 (3), fulvic acid 20 mg/dm^3 (4), bromide ions 20 mg/dm^3 (5).

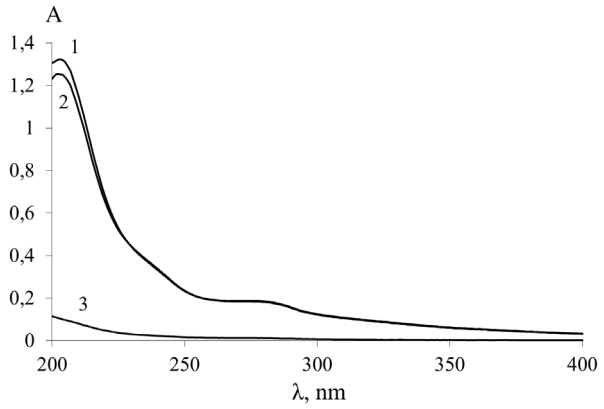

Fig. 3. Spectra of a solution of fulvic acid 20 mg/dm^3 (1), the same solution after passing through a cartridge Supelclean ENVI-18 (2), the same solution after passing through a cartridge SAX with the volume of 3 cm^3 (3).

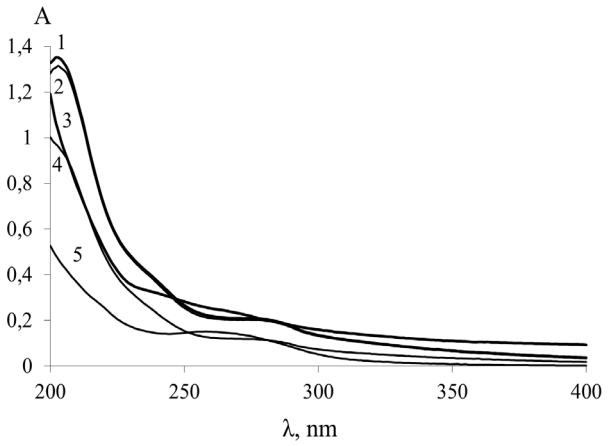

Fig. 4. Spectra of a solution of fulvic acid 20 mg/dm^3 (1), the same solution after passing through the cartridge Strata SDB-L (2), the same solution after passing through the cartridge LC Alumina-N (3), the same solution after passing through the cartridge XAD-2 or Polysorb-1 (4), the same solution after passing through the cartridge SAX with a volume of 1 cm^3 (5).

Also cartridges Silasorb SPH C8, Silasorb SPH C18, and DEAE-cellulose paper filter DE-81 were tested for fulvic acid removal from aqueous solution. The respective data is shown in Figures 5 and 6.

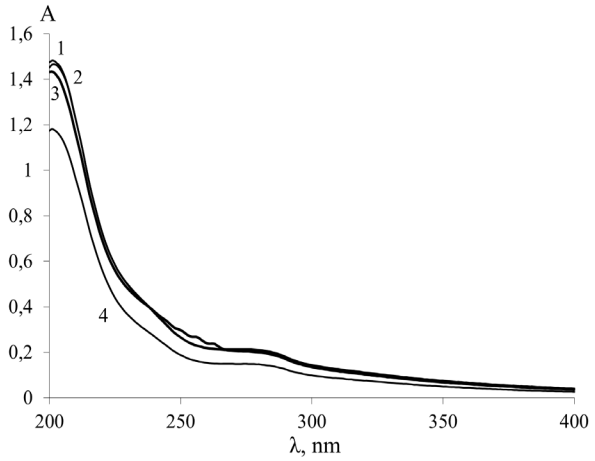

Fig. 5. Spectra of a solution of fulvic acid 20 mg/dm^3 (1), the same solution after passing through a cartridge Silasorb SPH C8 (2), the same solution after passing through a cartridge Silasorb SPH C18 (3), the same solution after passing through one layer of DEAE-cellulose filter DE-81 (4).

Figures 3-6 show that sorbents such as SAX and DEAE cellulose (as 5 layers of DE81 filter paper) effectively remove organic matter from the sample. After passing the samples through the sorbents Strata SDB-L, LC Alumina-N, XAD-2, Polysorb-1, the concentration of organic compounds in them changed slightly (Fig. 4). To check the effect of sorbents on the amount of bromide ions in water samples after sorption of organic matter, a photometric method was used to determine bromides with the increased sensitivity with the Phenol Red method [10]. Initially, photometric reaction was carried out with the solution containing 0.1 mg/dm^3 Br^- and the spectrum of this solution was recorded. Then 0.1 mg/dm^3 bromide solution was passed through the cartridge with SAX sorbent, photometric bromide determination reaction was carried out with filtrate, and the spectrum of the resulting solution was recorded.

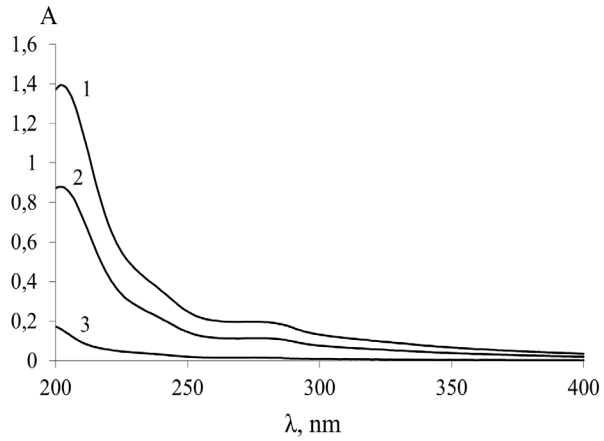

Fig. 6. Spectra of a solution of fulvic acid (1), the same solution after passing through two layers of DEAE-cellulose filter DE-81 (2), the same solution after passing through five layers of DEAE-cellulose filter DE -81 (3).

The results reveal that the peak at 590 nm, characteristic of bromide concentration of 0.1 mg/dm^3 (after the bromination reaction of Phenol Red), after filtering the sample through the sorbent SAX, disappears.

Sorption of bromide from aqueous solution as well as of mixture of bromide with fulvic acid was studied after passing these solutions through DEAE cellulose filter by means of the reaction of formation of Bromophenol Blue.

There was a practical absence of the bromide characteristic peak of Bromophenol Blue at $\lambda = 590$ nm after passing the bromide solution through the DE81 filter, and a sharp decrease in the bromide peak (up to 90 %) when passing solution containing Br^- and fulvic acid through the same filter.

It can be concluded that ion exchange sorbents SAX and DEAE-cellulose remove organic matter from the samples along with a large portion of bromide ions.

Spectra in the visible region after carrying out Phenol Red bromide detection reaction of the bromide solution as well as of the same solution after passing through a cartridge with Polysorb-1 and through a cartridge with XAD-2 resin were recorded.

After filtration through the porous polymeric sorbents Polysorb-1 and XAD-2 the bromide peak

remains almost unchanged, but these sorbents, as can be seen from Fig. 4, are not effective enough to remove organic substance (fulvic acid) from the sample.

Spectra of acidified samples

For efficient sorption of organic substances, the solutions of fulvic acid were acidified with sulfuric acid to pH 2.0, and then filtered through cartridges with reverse-phase sorbents. Fig. 7 shows the spectrum in UV region obtained for fulvic acid at a concentration of 20 mg/dm^3 at pH 2.0, as well as its spectrum after passing through the sorbents Supelclean LC-8 and Supelclean LC-18.

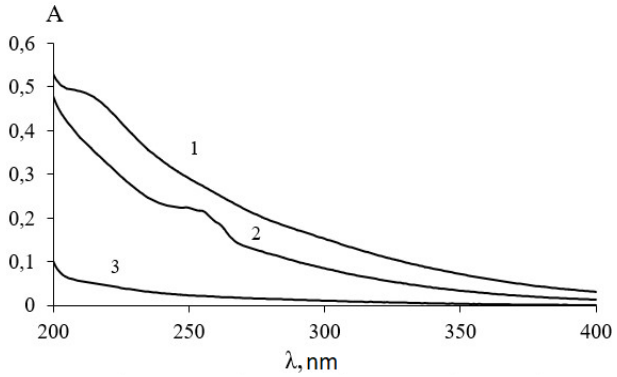

Fig. 7. Spectra in the UV region: 1 - fulvic acid 20 mg/dm^3 at pH 2.0; 2 - fulvic acid 20 mg/dm^3 at pH 2.0 after passing through a cartridge Supelclean LC-8; 3 - fulvic acid 20 mg/dm^3 at pH 2.0 after passing through a cartridge Supelclean LC-18.

Fig. 7 shows that the most effective for removing fulvic acid from the solution is the use of Supelclean LC-18.

The spectra recorded in the region 500 – 700 nm after carrying out the reaction of bromide with Phenol Red showed that the losses of bromide after filtration of samples containing bromide ions (0.1 mg/dm^3) and a mixture of bromide ions (0.1 mg/dm^3) with fulvic acid (20 mg/dm^3) through the sorbent Supelclean LC-18, are negligible (≤ 5 %).

Therefore, for the selective removal of organic compounds of natural origin from samples in which bromide ions are further determined, the use of Supelclean LC-18 sorbent may be recommended after acidification of the samples to pH 2.0. With the help of sorbent Supelclean LC-18 the interfering effect of 20 mg/dm^3 of fulvic acids was practically eliminated, the error of determination of bromide ions does not exceed 20 %. Acidification to pH 2.0 promotes the formation of molecular non-dissociated forms of organic compounds in solution, which are effectively separated from bromide ions on reverse-phase sorbents during solid-phase extraction.

Thus, to solve the problem of effective and selective removal of organic compounds from solutions containing bromide ions, it is advisable to first acidify the samples to pH 2.0, and then pass them through a column with sorbent of LC-18 type for further analysis for bromides by chromatographic or photometric methods [15]. Such sample pretreatment makes it possible to determine the content of bromide ions in waters which are characterized by a high content of organic compounds, in particular, turbid and colored waters.

Analysis of natural waters

To verify the suitability of the developed methodology for the determination of bromides using appropriate sample preparation, the natural groundwater of Odessa city (Jurassic horizon) and the Black Sea water, which was contaminated by oil spills, were analyzed. The results of the analyses are presented in the Table 1.

Table 1. The results of determining the content of bromides in groundwater and marine water by the proposed and reference methods (n = 3, P = 0.95).

Water	Oil found by IR-spectrometry, mg/dm^3	Bromide found by photometry with Phenol Red, mg/dm^3	Total bromine (Br) found by ICP-MS, mg/dm^3
Artesian, Odessa, Gagarina street	< 0.02	1.25±0.17	1.31±0.19
Artesian, Odessa, Academichna street	< 0.02	1.18±0.15	1.20±0.20
Artesian, Odessa, Fontanska Road	< 0.02	0.55±0.06	0.57±0.07
Artesian, Odessa, Admiral Avenue	< 0.02	1.24±0.16	1.23±0.18
Black Sea, Dolphin Beach, Odessa	0.04	39.5±1.3	40.1±1.5

The results showed that oil products concentration in contaminated sea water near Odessa city was 40 μg/dm^3; in the artesian waters of the Odessa city oil products were not detected. Seawater contamination with oil at the Dolphin Beach arose from oil spills near Odessa seaport. However, analysis confirmed that no penetration of oil products to artesian wells occured.

Seawater contains elevated concentrations of halides – chlorides, bromides and iodides, with typical bromide content of tens milligrams per litre. Elevated quantities of bromide are found in artesian wells of the city obviously due to partial infiltration of seawater into ground water.

It is seen from the Table that the concentrations of bromide in contaminated water obtained by photometric method after removal of organic pollutants by the proposed procedure satisfactorily coincide with the data on total bromine obtained by the ICP-MS method. This confirms the correctness of the proposed approach in the analysis of complex samples for bromides, given the fact that the concentration of total bromine in natural waters reflects the concentration of bromide ions, as bromate ions in natural waters are usually absent.

Conclusions

In order to selectively remove dissolved organic compounds from water matrix intended for analysis for bromide, sample acidification to pH 2.0 is recommended followed by sample filtration through the reverse-phase sorbent of LC-18 type. In these conditions 20 mg/dm^3 of fulvic acid characteristic of Dnipro river water are effectively separated from 0.1 mg/dm^3 Br^- with minimal losses of the latter. Results of natural water analysis by photometric and ICP-MS methods proved the applicability of the approach proposed.

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