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Correlation and digital signal processing techniques for the reduction of detection limits of bromate and bromide in model water samples by ion chromatography with direct ultraviolet detection

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Abstract

Bromate is a well known by-product produced by the ozonation (disinfection) of drinking water, of which the concentration is considered to be regulated to a low μg/l level. Successful ion chromatographic methods of determination involve the implementation of concentration columns. As an alternative to concentration, it is demonstrated that the low μg/l level can easily be attained using a simple and foolproof experimental arrangement of direct pseudo random injections of large quantities of the sample and ultraviolet (UV) detection at 204 nm with subsequent decorrelation of the detector signal. The approach, known as correlation chromatography, makes high demands to the reproducibility and other properties of the injection system. Although correlation chromatography is less sensible to spikes and baseline drift compared with normal chromatography, optimum results will be achieved by applying digital detector processing prior to decorrelation, combined with a proper modification of the eluent. This is demonstrated here. © 1997 Elsevier Science B.V.

Keywords: Digital-signal processing techniques; Signal processing; Bromate; Bromide

1. Introduction

Determination of low levels of bromate anions are of interest due to their possible carcinogenic properties [1]. Bromate appears as a possible by-product of the ozonation of bromide-rich waters (such as drinking water supplies from open sources located near the sea). Currently, the practical quantitation level for bromate in drinking water set by the US Environmental Protection Agency (US EPA) is 10 mg/l based on ion chromatographic techniques [2]. These methods have been modified and improved by using suppressed conductivity detection and concentration of bromate on concentration columns provided by Dionex. Determinations of concentrations below 0.5 mg/l were reported by several investigators [3,4].

The use of a concentration column involves specific problems: since natural waters always contain common anions like chloride, nitrate, sulphate, in quantities much larger than that of bromate, the concentration column will be saturated in a short time. Due to the presence other anions (like sulphate), bromate will be eluted from the concentration column before its concentration reaches detectable levels. The presence of chloride is especially disturbing because its band elutes very near to the bromate band when implementing common eluents like car-

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bonate or borate buffers. A large chloride peak will overlap and mask the small bromate peak, making the bromate quantitation impossible. To deal with this situation the chloride is removed from the sample before concentration of the bromate [3,4], by passing the sample through an On-Guard Ag cation resin (Dionex, Sunnyvale, CA, USA). In order to prevent the leached silver from this column reaching the concentrator or analytical column, a chelator column (MetPac CC-1, Dionex) was introduced between the sample loop and the concentrator column.

It follows from the description above that the sample concentration procedure is influenced by several factors which are difficult to control. In this context the equilibrium process of the concentration procedure causes extra difficulties when making judgements of the real concentration values, since the strongly retaining anions indeed ''drain'' out the sample of interest from the concentrator. An attractive alternative to concentration is a direct large amount of sample introduction to the column. The contemporary high efficiency columns enable introduction of 100–200 μl of the sample without significant deterioration of the resolution. Using direct injection, it was demonstrated that the EPA level for bromate quantification can be met with suppressed conductivity detection [5].

A completely different approach for the reduction of the detection limits is to implement multiple injection chromatography combined with digital detector signal processing. A special multiple injection technique has been applied: correlation chromatography (CC). CC was successfully applied in ion chromatography for the determination of common anions [6,7]. In CC the sample is introduced after short intervals according to a pseudo random binary sequence (PRBS). The detector signal is similar to a random function and as such can not be interpreted by human directly, but correlation of the detector signal with the input sequence results in a correlogram which is equivalent to a common single injection chromatogram, however with reduced noise. Assuming white noise, the noise reduction factor is about $\sqrt{k}/2$, where k is the number of injections made during the experiment. The noise reduction is about one order when the number of injections is several hundreds.

The disadvantage of CC is that it is quite demanding on the experiment conditions, especially the reproducibility of the injections. Since CC by its nature is an averaging procedure, the result is a mean value of the chromatograms obtained from hundreds of injections. However, deviations from the ideal situation, such as imperfect injections and nonlinearities lead to so-called ghost peaks and baseline disturbances, known as correlation noise. This makes CC difficult to use for the determination of low level sample components in the presence of high concentrations, because the correlation noise is proportional to the intensity of the peaks and large peaks will mask the presence of small ones. The other drawback of CC in its present form is a computational one: the decorrelation algorithm can only treat cases when the number of input sequence elements equals the number of measured signal values which makes it virtually impossible to decorrelate detector signals obtained by injecting large amounts of sample.

This paper shows that EPA detection levels can be attained with a simple and straightforward ion chromatographic system, using common UV detection and a computer controlled six-port sampling valve. The problem of the influence of a complex matrix is not considered in this paper, but the basic properties of the method are emphasised. The use of UV detection is especially advantageous, since chloride does not adsorb much UV radiation at the wavelengths used for the detection of bromate. However, it will be demonstrated that the required detection limit is difficult to achieve with a single injection alone and it is advantageous to combine this with CC. An attempt was made to solve the problem of correlation noise due to the fluctuating intensity of the injection peak and other large amplitude peaks by performing the bromate determination using a differential procedure [8]: certain amounts of the particular sample component were added to the eluent to reduce the overall intensity of the large peak which was not of interest.

A new sampling/decorrelation algorithm was developed to decorrelate the detector signal obtained by injecting large quantities of sample by a pseudo random sequence. The algorithm performs the necessary permutations of the detector signal values and it will be demonstrated that the resulting blocks of detector signals can be decorrelated by usual techniques. Because the detector signal is not allowed to

contain other parts than originating from the sample components, spikes, baseline oscillations and drift may deteriorate significantly the correlogram figure. Procedures were developed to remove the baseline drift and spikes from the detector signal. Low-pass Butterworth filtering was applied prior to the decorrelation to the detector signal to reduce baseline oscillations and high frequency noise.

2. Theory

The CC theory is exhaustively described in many papers and publications e.g., [9] and will be treated here only in the context of the present paper. In CC the sample is injected after a short interval of time Δt (0.1–2 s) according to the sequence, $\mathbf{x}=\{\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_n\}$, where n is the number of sequence elements. $\mathbf{x}_i$ has two values, 0 and 1, and depending on the particular value of the sequence element sample is introduced to the column if $\mathbf{x}_i=1$ or the sampling valve is not activated if $\mathbf{x}_i=0$. The time interval Δt is known as a clock period in CC [10]. The detector signal is digitised and recorded at $2n-1$ time moments by a personal computer, also with the interval Δt giving a sequence of the detector signal elements $\{\mathbf{y}_1,\mathbf{y}_2,...\mathbf{y}_{2n-1}\}$. Thus only one detector signal element value is recorded during the clock period. Let the correlogram vector be $\mathbf{h}=\{\mathbf{h}_1,\mathbf{h}_2,...\mathbf{h}_n\}$, then the relation between correlogram and detector signal elements will be a matrix equation

$$\boldsymbol{y}=\boldsymbol{X}\boldsymbol{h} \tag{1}$$

where $\mathbf{y}$ is the detector signal elements vector ranging from indices $n+1$ to $2n-1$, and $\mathbf{X}$ is a $n\times n$ circulant matrix whose first column is equal to $\mathbf{x}$ and the other columns are obtained from the first column by cyclic permutation of the first one. Eq. (1) can be easily inverted e.g., by fast Hadamard or Fourier transforms or by using direct decorrelation, since the matrix $\mathbf{X}$ has a formula for its direct inverse in closed form.

This approach assumes that the sample injection length is equal to Δt. In ion chromatography the eluent flow-rate is usually about 1 ml/min. When the digitisation interval Δt is about 1 s, the sample amount injected to the column is 1 s·(1 ml/min)=17 μl, which is far less than allowed by the resolution condition for a contemporary ion chromatographic column. To increase the injected sample amount, the sampling time must be increased to several, say $m\Delta t$, units and because a sampling valve in ion chromatography is usually a mechanical loop valve, several, say $l\Delta t$, units must be left for filling the loop. So, the whole clock period becomes equal $(l+m)\Delta t$ units of time. Here m and l are integers. It is rather straightforward to deduce that the input sampling sequence will be different in this case: every PRBS element will be replaced by $m+l$ elements, whose values are as follows: if $\mathbf{x}_i=1$, then it is replaced by m ones and l zeros, and if $\mathbf{x}_i=0$, then it is replaced by $m+l$ zeros. For example, a seven-element PRBS which is equal to $\tilde{\mathbf{x}}=\{111010\}$ becomes $\tilde{\mathbf{x}}=\{11100\ 11100\ 11100\ 00000\ 11100\ 00000\ 00000\}$. The decorrelation becomes a problem, however. The corresponding input matrix $\tilde{\mathbf{X}}$ is singular and unlike $\mathbf{X}$ it can not be inverted directly. It can be transformed easily to the block diagonal form and then inverted by a proper row and column permutation. The permutation matrix capable of performing this action has one non-zero element in each row and the column indices of the non-zero elements are spaced by $m+l$ units. For example, taking a three-element PRBS {110} and taking $m=2$ and $l=1$, the permutation matrix has the following structure

$$\boldsymbol{P}=\begin{bmatrix}1&0&0&0&0&0&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&0&0&1&0&0\\0&1&0&0&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&0&0&1&0\\0&0&1&0&0&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&0&0&0&0&0&1\end{bmatrix} \tag{2}$$

Performing left and right permutation of $\tilde{\mathbf{X}}$ one obtains a block diagonal matrix $\mathbf{X}_B$ as follows: $\mathbf{X}_B=\mathbf{P}\tilde{\mathbf{X}}\mathbf{P}^T$, where $\mathbf{P}^T$, denotes the transpose of $\mathbf{P}$. For our example it is as follows

$$\boldsymbol{P}\begin{bmatrix}1&0&0&0&0&1&1&0&1\\1&1&0&0&0&0&1&1&0\\0&1&1&0&0&0&0&1&1\\1&0&1&1&0&0&0&0&1\\1&1&0&1&1&0&0&0&0\\0&1&1&0&1&1&0&0&0\\0&0&1&1&0&1&1&0&0\\0&1&0&1&1&0&1&1&0\\0&1&0&0&1&1&0&1&1\end{bmatrix}\boldsymbol{P}^T=\begin{bmatrix}1&0&1&1&0&1&0&0&0\\1&1&0&1&1&0&0&0&0\\0&1&1&0&1&1&0&0&0\\0&0&0&1&0&1&1&0&1\\0&0&0&1&1&0&1&1&0\\0&0&0&0&1&1&0&0&1\\1&0&1&0&0&0&1&0&1\\1&1&0&0&0&0&1&1&0\\0&0&1&0&0&0&0&0&1\end{bmatrix}$$

or in block form

$$P\tilde{X}P^T = \begin{bmatrix} X & X & O \\ O & X & X \\ X & O & X \end{bmatrix}$$

From this example it follows that the block diagonal matrix contains two non-zero blocks in each ''block'' row and one block, **O**, where all elements are equal to zero. In general there will be m non-zero blocks and l zero blocks in each ''block'' row. Non-zero blocks are just equal to the matrix **X**, a common PRBS input matrix. Multiplying $\mathbf{X}_B$ with the $(m+l)n \times (m+l)n$ block diagonal matrix $\mathbf{X}_B^{-1}$, where on the diagonal block are $\mathbf{X}^{-1}$ matrices, results in a block matrix which non-zero blocks are identity matrices. In our example

$$X_B^{-1}(P\tilde{X}P^T) = \begin{bmatrix} X^{-1} & O & O \\ O & X^{-1} & O \\ O & O & X^{-1} \end{bmatrix} \begin{bmatrix} X & X & O \\ O & X & X \\ X & O & X \end{bmatrix} = \begin{bmatrix} I & I & O \\ O & I & I \\ I & O & I \end{bmatrix}$$

The decorrelation procedure is as follows: multiplying both sides of Eq. (1) with $\mathbf{X}_B^{-1}\mathbf{P}$ and recalling that for permutation matrices the transpose is also the inverse matrix, one obtains

$$\begin{aligned} X_b^{-1}Py &= X_B^{-1}\tilde{P}XP^T(Ph) = X_B^{-1}X_B(Ph) \\ &= I_B(Ph) \end{aligned} \quad (3)$$

where $\mathbf{I}_b$ is a block diagonal matrix which structure is similar to the $\tilde{\mathbf{X}}$, but the non-zero blocks are equal to the identity matrices. Thus instead of a normal correlogram (or chromatogram) **h**, the result of the proposed decorrelation procedure is a correlogram whose elements are the sum of the corresponding elements of correlogram. For the example in this paper it looks like

$$I_b(Ph) = \begin{bmatrix} 1 & & 1 & & & & & & \\ & 1 & & 1 & & & & & \\ & & 1 & & 1 & & & & \\ & & & 1 & & 1 & & & \\ & & & & 1 & & 1 & & \\ & & & & & 1 & & 1 & \\ 1 & & & & & & 1 & & \\ & 1 & & & & & & 1 & \\ & & 1 & & & & & & 1 \end{bmatrix} \begin{bmatrix} h_1 \\ h_4 \\ h_7 \\ h_2 \\ h_5 \\ h_8 \\ h_3 \\ h_6 \\ h_9 \end{bmatrix} = \begin{bmatrix} h_1 + h_2 \\ h_4 + h_5 \\ h_7 + h_8 \\ h_2 + h_3 \\ h_5 + h_6 \\ h_8 + h_9 \\ h_1 + h_3 \\ h_4 + h_6 \\ h_7 + h_9 \end{bmatrix} \quad (4)$$

Zero elements are omitted in $\mathbf{I}_b$. Note that indices in a correlogram vector are not ordered lexicographically but according to the permutation **P**. The resulting correlogram contains $n(m+l)$ elements which, as pointed out above, are sums of real correlogram elements. Also it must be back permutated to obtain intelligible results. Thus in this example the resulting correlogram would look like $\{\mathbf{h}_1+\mathbf{h}_2\ \mathbf{h}_2+\mathbf{h}_3\ \mathbf{h}_3+\mathbf{h}_1\ \mathbf{h}_4+\mathbf{h}_5\ \mathbf{h}_5+\mathbf{h}_6\ \mathbf{h}_6+\mathbf{h}_4\ \mathbf{h}_7+\mathbf{h}_8\ \mathbf{h}_8+\mathbf{h}_9\ \mathbf{h}_9+\mathbf{h}_7\}$.

Generalisation for any combination of n, m, l is straightforward. It follows that the proposed decorrelation algorithm acts as moving average filter over m elements, however with the peculiarity that the blocks of size $m+l$ are not ''mixed'' (e.g., elements $\mathbf{h}_3+\mathbf{h}_4$ and $\mathbf{h}_6+\mathbf{h}_7$ do not appear in the correlogram). Thus the chromatogram resolution will be reduced. This behaviour of the algorithm is not surprising, but it reflects mathematically the fact that the resolution (from the chromatographic point of view) is reduced already by performing a long injection.

3. Experimental

3.1. Equipment

First, commercially available valves were tested as sampling devices for correlation ion chromatography. Unfortunately, they could not withstand the requirements of CC for performing thousands of injections with an interval 1–5 s and broke down. Then the samples were introduced by the standard 6-port two-position valve with a Telrine rotor (Special Design Office, Estonian Academy of Sciences). The valve performance in correlation experiments was found to be acceptable. The rotor broke down after about fifty experiments (50 000 injections), so a replacement was necessary. Sample flow through the loop was established by a peristaltic pump (Zalimp, Poland). The eluent flow through the column was established by a common HPLC pump (Inkrom, Tallinn, Estonia). The guard column was an AG4A (Dionex, Sunnyvale, CA, USA). Dimensions: 4×50 mm, particle diameter: 13 μm. The separation column was an AS9-S6 (Dionex). Dimensions: 4×50 mm, particle diameter: 13 μm, capacity per column 30–35 μequiv., functional group: alkyl quaternary

ammonium, hydrophobicity: medium. Separated species were detected by an UV detector (Knauer Variable Wavelength Monitor) at the wavelength 204 nm. The experimental set-up is outlined in Fig. 1.

3.2. Chemicals

The eluent was an 11 m*M* borate buffer, pH 8.76 prepared in deionised water (Milli-Q). Models of drinking water samples were synthesised according to the specifications of mean Tallinn tap water (see Table 1) [11]. Note the absence of such common anions as carbonate and phosphate. Water samples were prepared from Na^+ salts instead of using cations found in Tallinn water. All salts were reagent grade purchased from Reachim, USSR or from Alltech. Several other parameters characterising contents of organic compounds and biological characteristics are regulated in Tallinn water, but were not taken into account in synthesising the model water samples since they could introduce uncontrollable interferences and are not relevant in the context of the present work. Composition of the synthetic tap water is presented in Table 1.

This model water sample was used as solvent for preparing bromate and bromide solutions of various concentrations. To avoid the appearance of a large amplitude water peak on the correlogram, borate buffer was added to the sample in such an amount that its concentration in the sample solution becomes equal to the eluent concentration. Elimination of the water peak was inevitable to avoid appearance of the correlation noise due to the variations of the water peak area.

Table 1
Concentration of anionic components of Tallinn tap water and in model samples

Ionic component	Concentration in Tallinn tap water	Concentration in synthetic tap water
HCO_3^-	127	120
Cl^-	18.5	18
SO_4^{2-}	128	128
F^-	0.22	–
NO_2^-	0.022	–
NO_3^-	5.28	5.2

3.3. Equipment control and data processing

The equipment control and data acquisition was performed by a ‘‘486’’ personal computer using an ADC-16 interface card (Keithley, USA). Actuating of the sampling valve was performed using laboratory-made software. Detector signal preprocessing and decorrelation was performed using laboratory-made subroutines in Matlab v4.b (MathWorks, Natic,

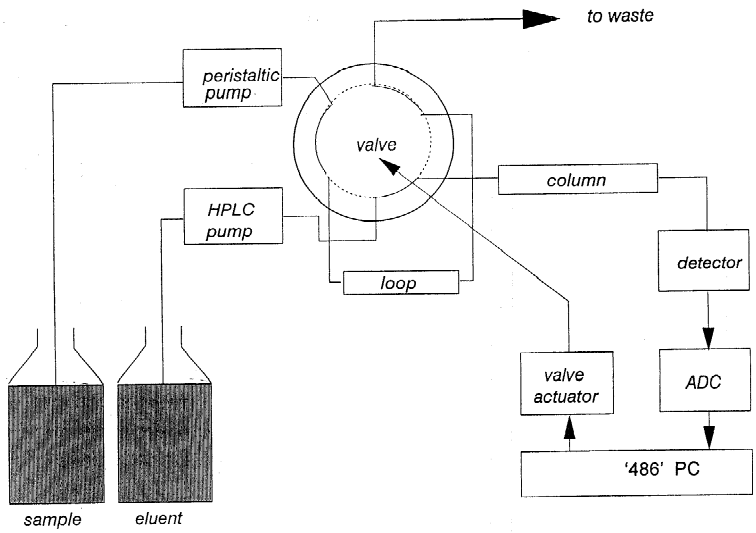

Fig. 1. Experimental set-up.

MA, USA). Data preprocessing included spike removal and baseline fitting by spline approximation.

4. Results

4.1. Performance of ion correlation chromatography

From a practical point of view either 127 element or 511 element sequences are of interest. Shorter sequences do not provide necessary reduction of the detection limit and longer sequences are time-consuming. If two 127 element PRBSs are used as the sampling sequence, the whole length of the experiment is about $2 \cdot 127 \cdot (10+4)/3600 \approx 1$ h. Expected improvement of the signal-to-noise ratio is by a factor of $\sqrt{127/2} = 5.6$. When using 511 element sequences, the experiment length is about 4 h and the improvement in signal-to-noise ratio is 11.3-fold.

The measurement procedure involved several stages:

(1) Injection of 128 (or 512) samples of size 8 (s)·1 (ml/min)=133 μl according to a pseudo random sequence was performed and the detector signal was recorded. (2) When the experiment was completed, the detector signal was filtered using a higher order Butterworth filter (a 5th order was chosen) with a cut-off frequency at about 15% of a maximum number of points on the power spectrum of the correlogram. The cut-off frequency was determined by analysing the power spectra of the detector signal at the point where the spectrum becomes flat. This procedure can be easily realised using standard MATLAB means and the details are not mentioned here. (3) The baseline subtraction was done with a cursor by pointing manually to the points on the correlogram where the baseline was supposed to pass. A spline function was passed through the selected points and subtracted from the detector signal. (4) Occasional spikes were removed in a similar way: the spike location was pointed by the cursor and then automatically zoomed on the PC screen. Beginning and end points of the spike were pointed by the cursor again and a MATLAB routine interpolated a line between those points. This line replaced the spike area in the detector signal. (5) Decorrelation was performed by a subroutine performing the decorrelation algorithm outlined in the Section 2. The inversion of was performed by a standard fast Fourier deconvolution procedure instead of the theoretically more efficient fast Hadamard transform for which MATLAB has no convenient facilities. The detector signal preprocessing stages are illustrated in Fig. 2.

For comparison the correlogram without any data preprocessing action is given. It is evident from Fig. 2 that the correlogram without data preprocessing is not intelligible, thus indicating the importance of this action in CC.

To test the performance of CC for the bromide and bromate determination the known bromide and bromate salts were dissolved in eluent. The lowest concentration of bromate that can be detected by UV detection combined with CC is about 5 μg/l. For bromide it is about one-order less: 0.5 μg/l. The sampling time was 8 s and the interval left for filling the loop was 4 s (the sample was pumped through the 140 μl loop with a flow-rate of 7 ml/min to ensure complete filling of the loop between injections). The corresponding correlogram is given in Fig. 3. CO_3^{2-} peaks have a different direction towards the baseline in this and in the following figures, because it was difficult to control the solubility of atmospheric CO_2 in equal amounts both in sample and eluent vessel. The reproducibility of the determination of bromide and bromate peak areas were estimated to be equal to 3.4% and 2.4%, respectively.

It follows from Fig. 3 that the EPA demand for the determination of bromate below 10 μg/l can not be easily met just by a large volume single injection alone (without preconcentration), while this can be done with CC without any major problems. Calibration lines for both anions are shown in Fig. 4. In this Figure no slope jump can be detected at the point where CC determinations of the concentration turn to single injection determinations.

The correlation coefficients of the calibration lines are 0.999 and 0.998 for bromate and bromide, respectively. The detector wavelength was found to be optimal and no attempts were made to further optimise the detection wavelength.

4.2. Masking of the interferences

Although the results presented in Section 4.1 look promising, they are valid for the non-realistic case of

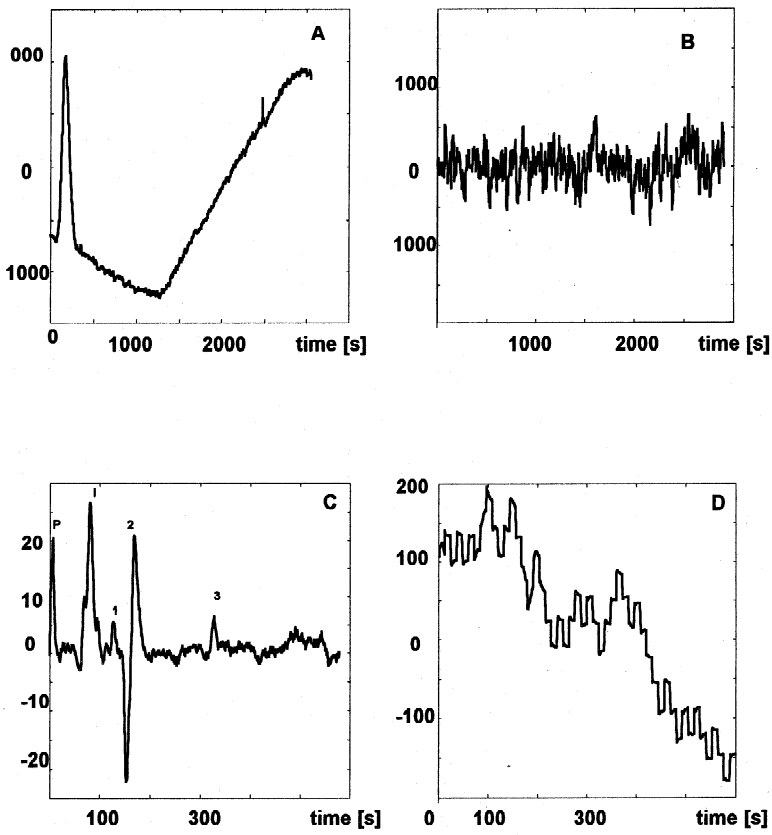

Fig. 2. Illustration of the data preprocessing and decorrelation procedures. (A) Detector signal with spike and baseline drift. (B) Detector signal after compensation for spike and baseline drift. (C) Correlogram, peaks: P pressure, I injection, 1 bromate, 2 carbonate, 3 bromide. (D) Correlogram from unproceeded detector signal.

samples of single ion solutes in the eluent solution, which concentration is carefully balanced with that of the eluent concentration itself. So the experiments were continued with synthetic water samples. As pointed out already in Section 1, the main interference for the bromate determination is chloride which peak overlaps with the bromate peak. Chloride is considered as UV nonactive at 204 nm. Nevertheless, we found that it has a certain adsorption also at 204 nm and when in large amounts it can mask the bromate peak (see Fig. 5a).

The intensity of the chloride peak was reduced by adding the corresponding amount of chloride to the eluent. The result is demonstrated in Fig. 5b. The procedure is rather efficient in separating the bromate from its main disturbance. No deterioration in column performance was observed due to the passage of the eluent containing high amount of common anions. Those anions should affect as eluent anions in the case of differential measurement (i.e., they compete with the sample anions for the anion-exchange sites of sorbent). Retention times on the correlogram should be different compared with the single injection chromatogram. This phenomenon was not significantly observed in the present work (compare e.g., Fig. 3a Fig. 3c, or Fig. 3b Fig. 3d, or Fig. 5a Fig. 5b) as it was in our previous works [6,7].

Apart from the reduction of the intensity of the chloride peak, the reduction of the intensities of the large peaks which do not overlap with the bromate peak but of which the area determination is not of interest, is crucial in CC since deviations in injected quantities from the mean value generate correlation noise. There are also other sources of correlation noise of which the mechanism is not clear yet, but probably can be attributed to the large intensity

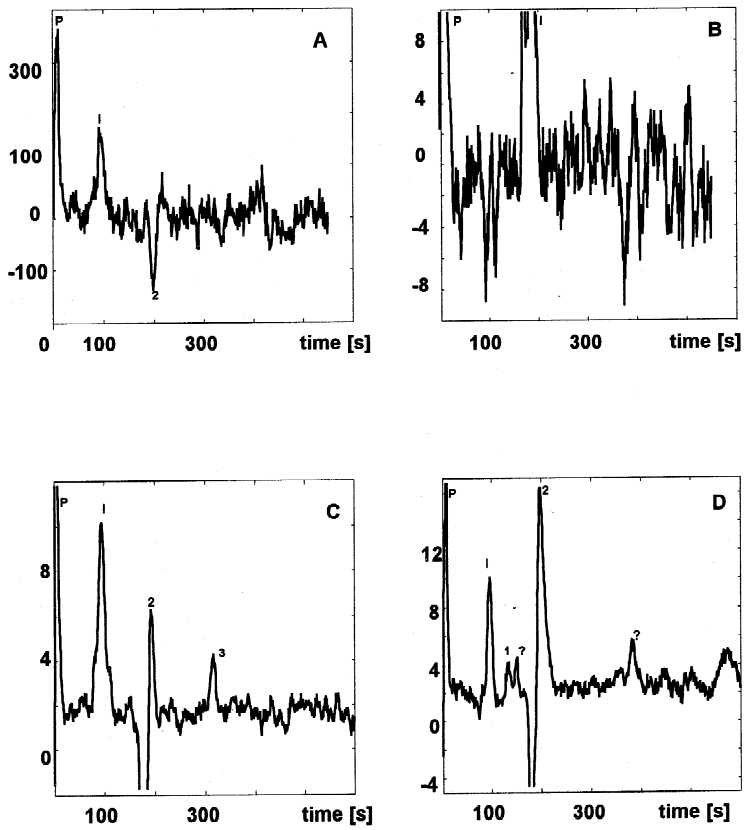

Fig. 3. (A) Single injection of 3 μg/l bromide. (B) Single injection of 20 μg/l bromate. (C) Correlogram of 0.2 μg/l bromide. (D) Correlogram of 5 μg/l bromate. Peaks: p pressure, I injection, 1 bromate, 2 carbonate, 3 bromide, ? unknowns.

peaks. Correlation noise will mask small peaks in the correlogram. In Fig. 6 a demonstration of this phenomenon is presented.

Fig. 6a shows a single injection chromatogram of a water sample spiked with 10 μg/l bromate. No bromate peak can be detected in the chromatogram. A correlogram of the same sample is presented in Fig. 6b. Although the major peaks can be recognised easily, the baseline noise amplitude is significantly worse than in the single injection chromatogram. In Fig. 6c the correlogram of the same sample is presented in the case when hydrocarbonate, carbonate, chloride and nitrate ions were added to the eluent in concentrations found in the sample. Both sample and eluent contained also a sulphate ion to keep the ionic strength of the sample near to the real water samples. However, its peak is invisible since it is UV nonactive.

Fig. 6c shows that the reduction of the large amplitude peaks is possible, thus enabling detection of the bromate peak. Comparing the intensity of the peak 1 on correlogram with the mean level of the noise power (estimated e.g., between 300–400 s) one can conclude that the peak can be visually detected and thus be considered as being just on the detection limit. Also, as one can notice by observing the correlogram several peaks (of unknown origin) have been detected by CC technique. Now the correlation noise is also reduced in proportion of the reduction of the peak amplitudes, and the dominating noise on the detector signal is the common noise of the baseline, which is suppressed by the correlation procedure. The detection limits as reported in Section 4.1 were not obtained, since the determination of bromate is now in fact a differential measurement against the eluent that contains absorbing ions. Such

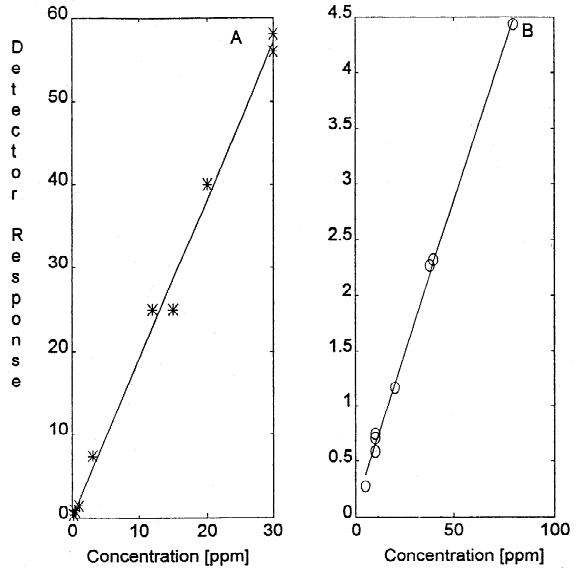

Fig. 4. (A) Calibration line for bromide determination, single injection measurements cover concentration range above 10 ppm, CC measurements cover concentration range below 5 ppm. (B) Calibration line for bromate determination, single injection measurements cover concentration range above 50 ppm, CC measurements cover concentration range below 50 ppm.

a procedure always involves extra noise. The bromate concentration that was eventually measured was 10 μg/l, meeting EPA requirements.

5. Discussion

It follows from the results that reasonable procedures for bromate determination could be developed using common HPLC equipment, thus making the determination of bromate accessible to the laboratories lacking contemporary expensive ion chromatographic equipment. However, the methodology was not yet tested on real local surface water samples (e.g., the supply of Tallinn city water is the Ülemiste Lake). The approach of using synthetic water samples was taken intentionally to avoid possible interferences and complications that might arise from the possible biological contamination of the water from algae and the presence of the organic compounds. Both interferences can be removed by standard techniques, which application was beyond the interest of the present work.

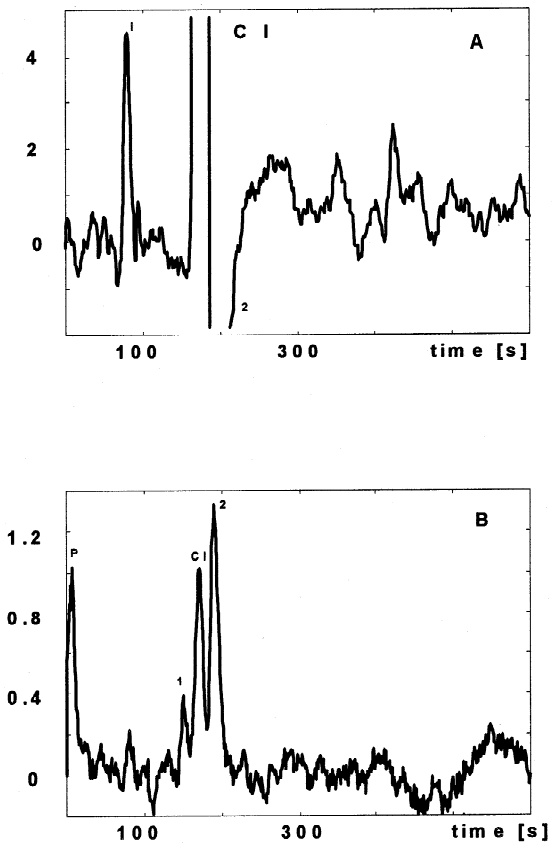

Fig. 5. Ion chromatogram of bromate and chloride ions, concentrations 25 mg/l Cl^-, 5 μg/l BrO_3^-. (A) Eluent without chloride added. (B) Concentration of chloride in eluent is 24 mg/l. Peaks: P pressure, I injection, 1 bromate, 2 carbonate, Cl chloride.

Disadvantages of the CC approach are that it needs more sample and time. The first is not a major problem, since samples and chemicals involved are cheap. The long duration of the experiments is also not a big problem generally, since the whole procedure is automated.

The usual objection to CC —sophisticated procedure and equipment— also does not seem to be relevant, since the equipment involves commercially available parts (air actuated sampling valve, PC control of the measurements), which all are present in a contemporary HPLC laboratory, and the whole set up is simple compared with the use of several sorbents for removing chloride, chelating silver and concentration of the sample. Direct determination of

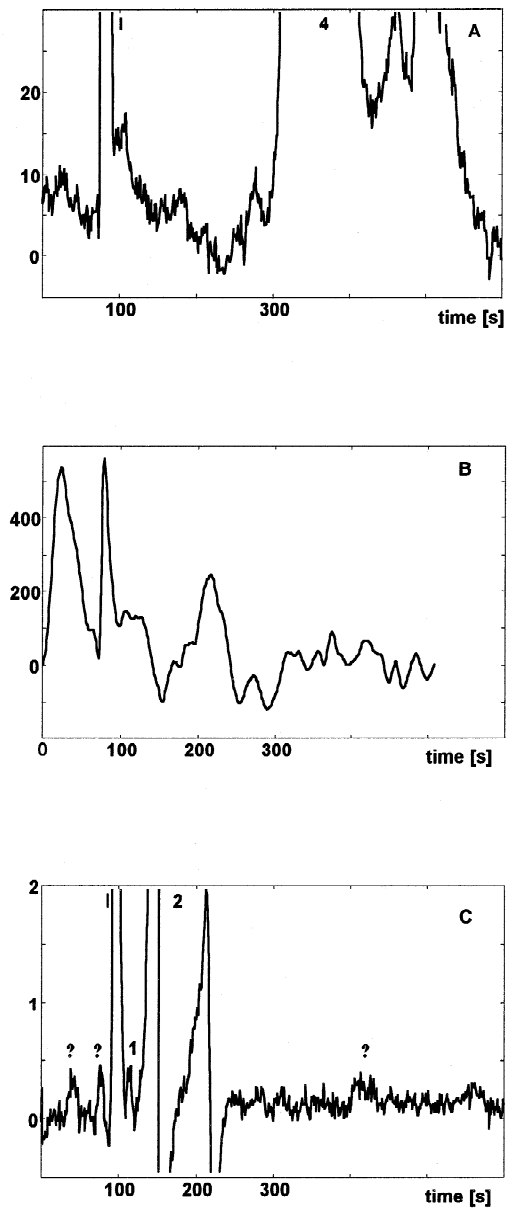

Fig. 6. (A) Single injection chromatogram of a model water sample spiked with 10 mg/l bromate. (B) A correlogram of the same sample. (C) Correlogram of the same sample in the case of addition of hydrocarbonate, carbonate, chloride and nitrate ions to the eluent in equal concentrations as found in the sample. Peaks: I injection, 1 bromate, 2 carbonate, 4 nitrate, ? unknowns.

the sample versus concentration is always a preferable procedure. Although concentration results are frequently accompanied with recovery studies confirming the reliability of this procedure, recent studies indicate that concentration procedures involve sophisticated equilibrium processes between competing species for the adsorption sites on the sorbent, and the desorbtion result (especially concentrating low concentration samples) might differ considerably from the amount of the species present in the sample.

Sophisticated data processing procedures are conveniently performed by MATLAB software. Major problems with CC which required main involvement was the development of the experiment control software. Since MATLAB does not provide any means for controlling events in real time, the Keithey interface card had to be programmed in Basic or C languages.

6. Conclusions

Bromate anions are difficult to determine in concentrations below 10 μg/l using common HPLC equipment, UV detection and single injection of a large quantity of sample, which do not yet discard resolution because the result is below the detection limit of the determination. CC proves to be successful in the determination of bromate. However, it requires detector signal preprocessing and masking of large peaks of the disturbing common anions. This can be achieved by adding a corresponding amount of common anions to the eluent, thus making the determination of bromate a differential measurement.

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