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Improvement of a computer program for the ion chromatographic determination of some anions in natural waters

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Abstract

A previous computer program for the optimum ion chromatographic determination of fluoride, chloride, bromide, sulphate, nitrite, nitrate and hydrogenphosphate in waters was applied to conductivity detection. In this work the abilities of a spectrophotometric detector especially for the determination of bromide, nitrite and nitrate at lower concentrations were systematically examined and incorporated into the program. The new program permits the planning of the analysis with UV detection, and also the prediction of the most appropriate detector for the determination of these three anions in different individual water samples.

1. Introduction

Computer-assisted procedures described in the literature are mostly concerned with the optimization of the eluent composition and separation [1,2], but there are also other parameters that have to be optimized for the successful determination of anions in natural waters. Our previous computer program [3] facilitates the selection of detector output ranges and permits the planning of the determination of fluoride, chloride, nitrite, bromide, nitrate, hydrogenphosphate and sulphate with conductivity detection, and the method development is thus rapid and highly efficient. The measurement of conductivity is the most general method of detection for the ion chromatographic determination of anions. In

different types of natural waters (*e.g.*, precipitates, tap water, sea water, mineral waters) these anions appear in different concentrations and different concentration proportions. In many instances the great concentration differences between individual anions prevent the successful determination of all the anions, especially those present at lower concentrations. The use of an additional spectrophotometric detector which permits the detection of nitrite, bromide and nitrate often increases the number of anions that can be successfully determined in natural waters by ion chromatography.

The aim of this work was the adaptation of the previous computer program [3] for the use of two different detectors. The structure of the program was modified and two additional databases were constructed on the basis of statistically evaluated results of several systematic ion

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chromatographic experiments with spectrophotometric detection.

2. Experimental

2.1. Apparatus and experimental conditions

All the experiments were carried out on a Dionex 4000i ion chromatographic apparatus with a Dionex variable-wavelength detector (Dionex, Sunnyvale, CA, USA). The system consisted of an AG4A guard column, an AS4A separation column and an anion micromembrane suppressor after which the detector flow cell was inserted. The injection volume was 50 μ l, eluent flow-rate 2.0 ml/min, regenerant sulphuric acid concentration 12.5 mmol/l, regenerant flow-rate 2.8 ml/min and applied wavelength 190–217 nm. An SP 4290 integrator (Spectra-Physics, San Jose, CA, USA) was used.

2.2. Reagents and procedures

All solutions and eluents were prepared from analytical-reagent grade chemicals using deionized water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Sodium hydrogencarbonate was purchased from Merck (Darmstadt, Germany). All other chemicals [Na_2CO_3 , NaNO_2 , NaNO_3 , NaBr and H_2SO_4 (96%, 1.84 kg/l)] were purchased from Kemika (Zagreb, Croatia). Two stock solutions, 100 mmol/l NaHCO_3 and 100 mmol/l Na_2CO_3 were used to prepare the eluent, 1.7 mmol/l NaHCO_3 –1.8 mmol/l Na_2CO_3 .

2.3. Basic experiment

Chromatographic responses at different wavelengths were examined with the aim of building up an experimentally based database and with the aim of checking the maximum absorption for nitrite, bromide and nitrate. The areas and heights of chromatographic peaks of injected solutions with anion concentrations of 1 mg/l were measured for a detector output range of 0.02 absorbance at 23 whole-number wave-

lengths between 190 and 217 nm. The maximum absorption was obtained at 190 nm for bromide, 203 nm for nitrate and 211 nm for nitrite and the further experiments were performed at these wavelengths.

In the main experiment, six detector output ranges from 0.002 to 0.1 absorbance were examined in order to find usable calibration functions for nitrite, bromide and nitrate. Concentrations of the calibration solutions were selected in accordance with the composition of natural waters and extended from 0.008 to 4.9 mg/l for nitrite, from 0.021 to 4.5 mg/l for bromide and from 0.001 to 6.4 mg/l for nitrate. Approximately 700 experiments were done.

Calibration functions for a selected anion in a selected detector output range were obtained by measuring the areas or heights of the chromatographic peaks from at least seven calibration solutions of different concentrations. Each solution was injected at least twice. Concentrations of the calibration solutions were chosen so that the measured chromatographic peaks extended over the whole detector output range and so that the first and the last calibration solutions would serve as an indication of the anion concentrations that could be determined in a certain detector output range. All the measurements were done at the wavelength of maximum absorption. Under our experimental conditions bromide was not determinable in the lowest detector output range of 0.002 absorbance.

2.4. Statistical evaluation of results

For each set of measurements the regression line $y = a + bx$ and related statistical parameters were calculated, where y is peak area or peak height and x is the concentration of anions.

3. Results and discussion

The improvement of the previous computer program [3] consisted of three stages. In the first stage, two additional experimentally obtained databases connected with UV detection were constructed. Second, the structure of the pro-

gram was adapted to the use of a UV detector. Finally, three new blocks of computer program were added. The operation of the modified program is illustrated on two examples with different natural water samples.

3.1. Computer-assisted procedures

The structure of the first database for a UV detector is similar to existing database for a conductivity detector [3]. It includes eleven statistical parameters for each calibration graph ($y = a + bx$) as follows: n = number of calibration points; x_1 = the lowest concentration of calibration solution; x_n = the highest concentration of calibration solution; \bar{x} = mean of the x values (concentrations); \bar{y} = mean of the y values (peak areas or heights); a = intercept; s_a = standard deviation of the intercept; b = slope; s_b = standard deviation of the slope; r = correlation coefficient; and $s_{y/x}$ = standard error of the estimate. The total number of data points is 374.

The second new database consists of responses of the UV detector for nitrite, bromide and

nitrate at different wavelengths between 190 and 217 nm. Variables $\gamma\lambda$ and $\gamma\lambda_{\max}$ were introduced. This database was constructed in order to allow the use of the first database for analyses at wavelengths that differ from those with maximum absorption. The reason is that in reality the measurements for nitrite, bromide and nitrate are not always done at the wavelengths of the maximum absorption [4,5] and that different workers quote different λ_{\max} values [6,7].

A database with statistical F factors for different degrees of freedom and a 0.05 significance level was also added [8].

The structure of the improved program is shown in Fig. 1. The four real starting positions (four triangles in Fig. 1), known peak area, known peak height, approximately known concentration or the prior choice of a certain detector output range remained the same. There are three new blocks, H, I and J. The main functions of blocks A, B, C, D, E, F and G were described previously [3]. No global changes were made to these blocks, but their detailed structure and also some data inputs shown in Figs. 2-5 were modified. The changes are orientated toward the

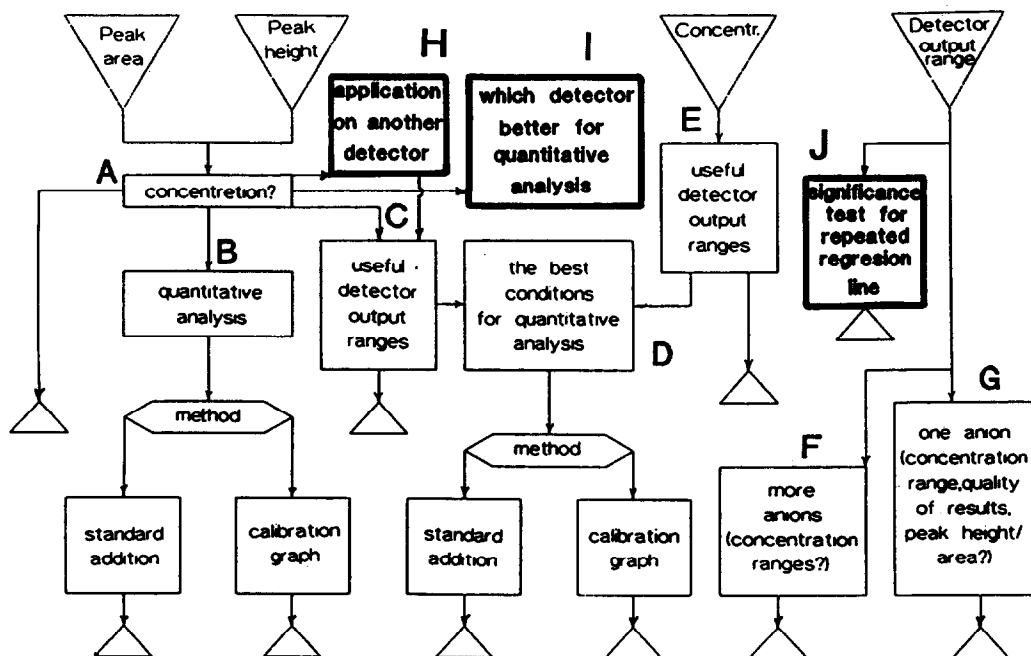


Fig. 1. The main structure of the improved computer program.

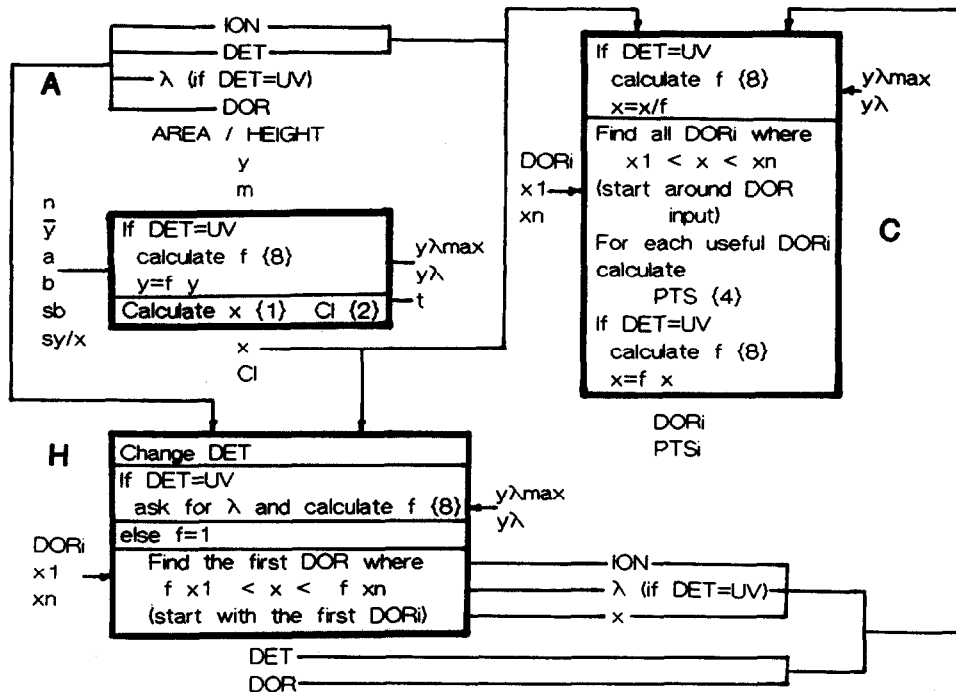


Fig. 2. The main operations, data inputs and data outputs for blocks A, C and H.

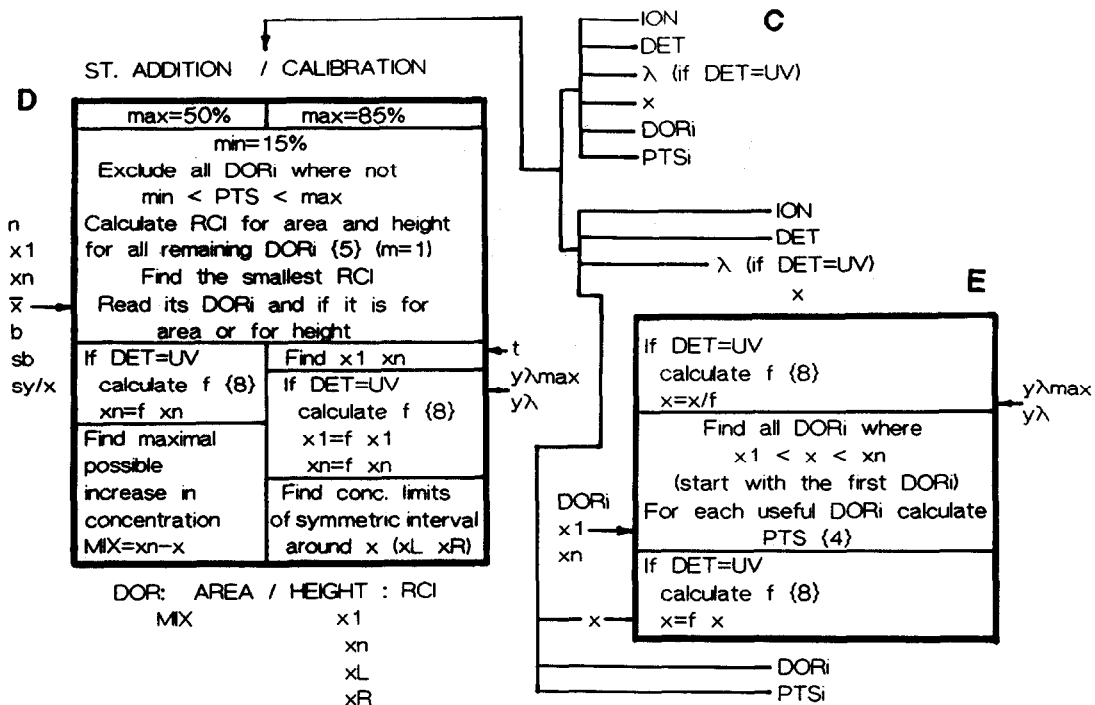


Fig. 3. The main operations, data inputs and data outputs for blocks D and E.

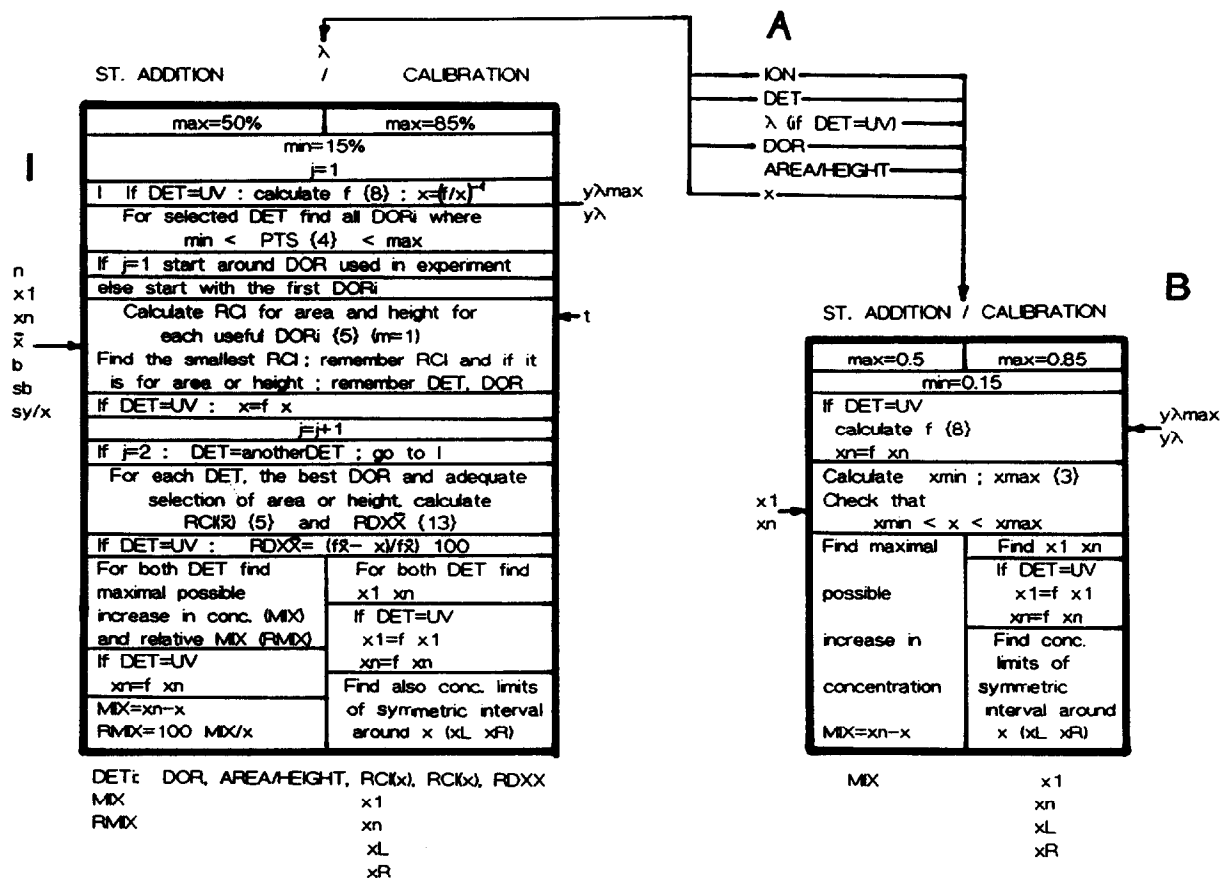


Fig. 4. The main operations, data inputs and data outputs for blocks B and I.

use of another detector also at wavelengths that differ from λ_{\max} . The additional variables DET, λ , $y\lambda_{\max}$ and correction factor f were used. Relative confidence intervals (RCI) for UV detection were also calculated for λ_{\max} .

For understanding the detailed structure of the program, general principles have to be described. Each block is represented by a rectangle. All the data necessary for the operation of the individual blocks are shown in figures. Data from the main two files for UV and conductivity detection are on the left-hand side of the rectangle. The data from the file that allows the corrections of results if the wavelength used differs from λ_{\max} , the file with t factors and the file with F factors are on the right-hand side. The user must input the data at the top, and output data are found at the bottom. The main se-

quences of the operations are described on each rectangle. The numbers of necessary mathematical relationships are stated in brackets.

The list of mathematical relationships used by the program is as follows:

$$\{1\} \quad x = \frac{y - a}{b}$$

$$\{2\} \quad \text{CI} = \frac{s_{y/x} \cdot t}{b} \left[\frac{1}{n} + \frac{1}{m} + \frac{(y - \bar{y})^2 s_b^2}{b^2 s_{y/x}^2} \right]^{1/2}$$

$$\{3\} \quad x_{\min} = \min x_n, \quad x_{\max} = \max x_n$$

$$\{4\} \quad \text{PTS} = \frac{x}{x_n} \cdot 100$$

$$\{5\} \quad \text{RCI} = \frac{s_{y/x} \cdot t \cdot 100}{x \cdot b} \left[\frac{1}{n} + \frac{1}{m} + \frac{(x - \bar{x})^2 s_b^2}{s_{y/x}^2} \right]^{1/2}$$

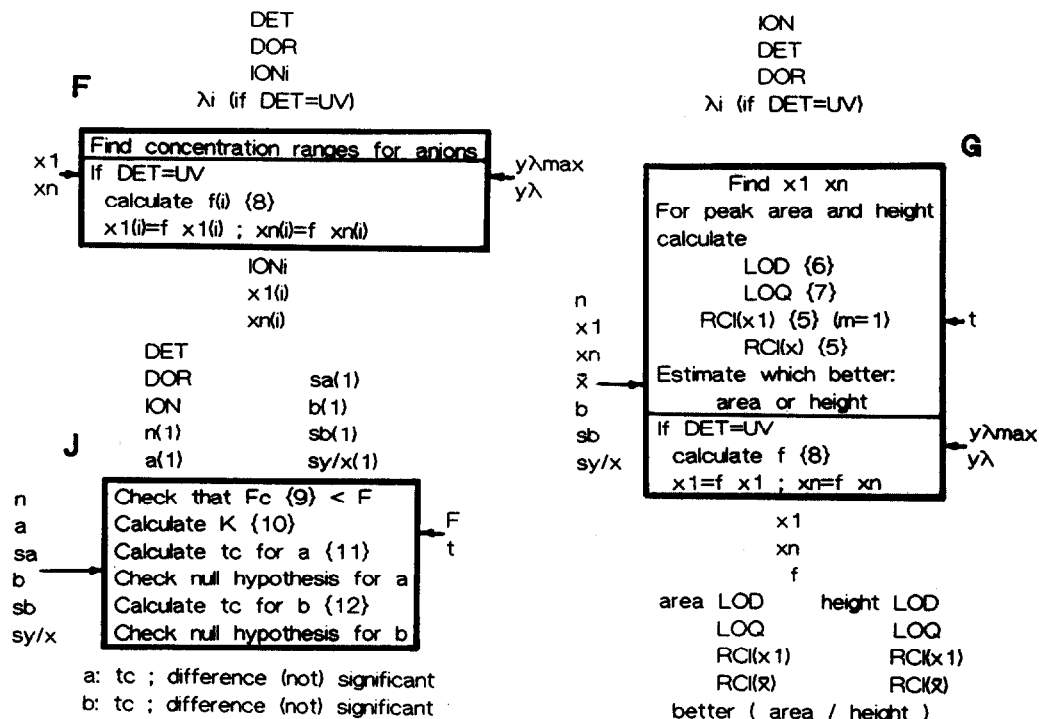


Fig. 5. The main operations, data inputs and data outputs for blocks F, G and J.

$$\{6\} \text{ LOD} = \frac{3s_{y/x}}{b}$$

$$\{7\} \text{ LOQ} = \frac{10s_{y/x}}{b}$$

$$\{8\} f = \frac{y\lambda_{\max}}{y\lambda}$$

$$\{9\} F_c = \left(\frac{\text{greater } s_{y/x}}{\text{smaller } s_{y/x}} \right)^2$$

$$\{10\} K = \left[\frac{s_{y/x}^2(n-2) + s_{y/x_1}^2(n_1-2)}{n+n_1-4} \right]^{1/2}$$

$$\{11\} t_c = \frac{|a - a_1|}{K \left(\frac{s_a^2}{s_{y/x}^2} + \frac{s_{a_1}^2}{s_{y/x_1}^2} \right)^{1/2}}$$

$$\{12\} t_c = \frac{|b - b_1|}{K \left(\frac{s_b^2}{s_{y/x}^2} + \frac{s_{b_1}^2}{s_{y/x_1}^2} \right)^{1/2}}$$

$$\{13\} \text{ RDX}\bar{X} = \left| \frac{\bar{x} - x}{\bar{x}} \right| \cdot 100$$

The meanings of the symbols that appear in the above mathematical relationships and in the figures are as follows:

CI	= confidence interval;
DET	= detector;
DOR	= detector output range;
f	= correction factor;
F_c	= calculated F factor
ION	= anion;
LOD	= limit of detection;
LOQ	= limit of quantification;
m	= number of repeated measurements;
MIX	= maximum increase in concentration;
PTS	= % of total scale on which chromatographic peak appears;
RCI	= relative confidence interval;
RDX \bar{X}	= relative deviation of x from \bar{x} ;
RMIX	= relative MIX;
t_c	= calculated t factor

- x_L = lower concentration limit of symmetric concentration interval around x ;
 x_R = upper concentration limit of symmetric concentration interval around x ;
 y_λ = response of UV detector for selected anion at selected λ ;
 $y_{\lambda_{\max}}$ = response of UV detector for selected anion at λ_{\max} .

The subscript i shows that there are more data of the same type.

The first newly introduced block H is a sort of interface. It is useful when a preliminary experiment was carried out with one detector. The estimation of concentration was made on the basis of this experiment. However, it is evident that this detector does not represent a good solution and we would like to carry out the optimization procedure (blocks C and D) with another detector. Block H changes the value of the variable DET and asks for λ if the detector is a UV type. It finds the first useful detector output range DOR, which is essential for the operation of block C.

With the introduction of block H and with the changes in blocks A–G, the program became suitable for the predictions and planning of the analysis with spectrophotometric detection. However, block I allows the comparison of the abilities of both detectors for the determination of bromide, nitrite or nitrate in a specific water sample (Fig. 4). It also helps in planning the quantitative analysis for both detectors with the method of standard additions (MIX, RMIX) or with a calibration graph (x_1 , x_n , x_L , x_R). It predicts the best detector output range and the best conditions (the measurement of area or height) for each detector. The quality criterion is the relative confidence interval (RCI) calculated for the estimated concentration. For an easier and more appropriate decision for one of the two detectors, the program reports some other parameters. The concentration ranges for suggested detector output ranges are not the same for both detectors. Therefore, RCI for \bar{x} are calculated. The relative deviation of estimated concentration from \bar{x} is also important. The new

more comparable parameter RMIX was introduced.

Block J offers the possibility of occasional checking of the agreement of repeated calibration functions with data from databases. The significance test for a and b has been described [9]. The equations were modified in such a manner that they permit the calculations with parameters that are saved in computer databases.

3.2. Examples of application

The operation of the modified program is illustrated on examples with different natural water samples. In the first instance we had determined the concentration of bromide in drinking water. The determination of bromide is not always possible with conductivity detection. Therefore, we decided to use a UV detector. The wavelength was 190 nm. A preliminary experiment was carried out at the lowest detector output range (0.005 absorbance). The concentration was estimated from the measured peak area with the aid of block A. The results were $x = 0.054$ mg/l and $CI = 0.012$ mg/l.

In the next stage the selection of DOR was checked. With block C all useful detector output ranges with related percentages of the total scale on which the chromatographic peaks appear were found. These are 0.005 absorbance (PTS = 30.0%), 0.01 absorbance (PTS = 13.6%) and 0.02 absorbance (PTS = 6.0%). Block D was selected for the planning of quantitative analysis under the optimum experimental conditions. We decided to use the method of calibration function. The computer suggested the DOR 0.005 absorbance and the measurement of height which has a lower confidence interval. The reported value of RCI was 22.7%. Other predictions were $x_1 = 0.021$ mg/l, $x_n = 0.190$ mg/l, $x_L = 0.021$ mg/l and $x_R = 0.087$ mg/l. Quantitative analysis was carried out under predicted conditions. The determined concentration was 0.057 mg/l and it shows very good agreement with the computer estimation (0.054 mg/l).

The prediction that the measurement of peak height offers better results was checked. We calculated RCI for the measurement of peak area and peak height. The former value was 29.8% and the latter 17.2%. The conclusion is the same as in the prediction. This example illustrates the operation of blocks A, C and D which were adapted for the use of a UV detector.

We also wanted to check if the calibration functions (area-concentration, height-concentration) with four calibration points, which was used for the determination of bromide in drinking water, differed significantly from those in the database. Block J was used. For the relationship between peak area and concentration the values of tc were 0.18 for a and 0.62 for b . The related parameters for the measurements of peak height were 1.27 and 0.83. No one value exceeded the critical value of 2.31 for the t -test ($p = 0.05$).

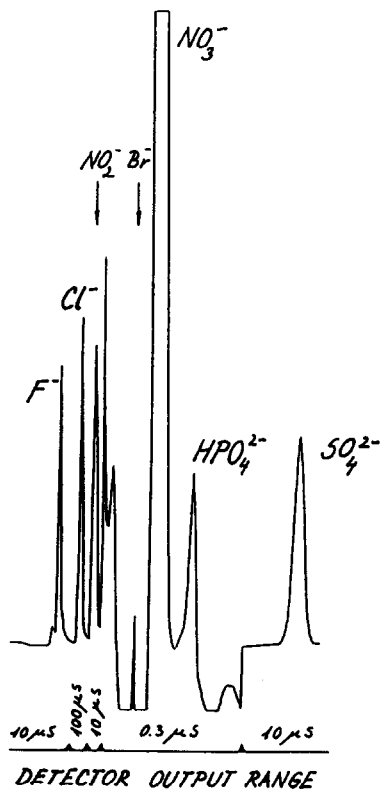


Fig. 6. Chromatogram of mineral water with conductivity detector.

The program reported that there is no significance difference within each pair of calibration functions.

Figs. 6 and 7 show chromatograms of mineral water with conductivity and UV detection, respectively. Also in this instance bromide cannot be successfully determined with a conductivity detector; the baseline is unstable and out of range. In this sample of mineral water the determination of nitrite is possible with both detectors. We would like to know which is better in this situation; block I can help. The concentration estimated with block A was 1.8 mg/l, λ was equal to λ_{\max} and the method of standard additions was selected. The report of block I is represented in Table 1.

The program suggests the measurement of peak height with the conductivity detector and peak area with the UV detector. Conductivity detection also permits a greater increase in concentration. Therefore, we decided to use the conductivity detector. We prepared five solutions with different standard additions. The determined concentration of nitrite was 2.8 mg/l. To

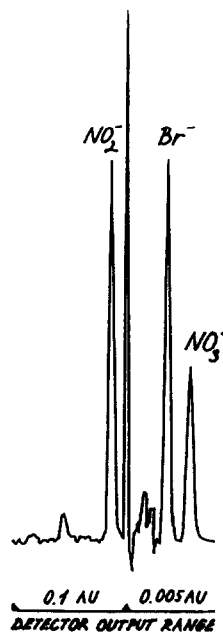


Fig. 7. Chromatogram of the same mineral water as in Fig. 6 with UV spectrophotometric detector.

Table 1
Report of the computer program when block I was used

Parameter	Detector	
	Conductivity	UV
DOR	10 μ S	0.1 AU
Area/height	Height	Area
RCI(x)	9.1%	22.3%
RCI(\bar{x})	8.9%	22.0%
RD \bar{X}	46.5%	29.3%
MIX	4.6 mg/l	3.1 mg/l
RMIX	256%	172%

check the prediction of the more appropriate detector, the experiment was repeated with the UV detector, and confirmed the prediction. The relative confidence intervals obtained were 62.0% for peak height and 97.7% for peak area.

This example with mineral water also illustrates that the use of the improved program allows more successful planning and more complete analysis of the anions in natural waters. Fig. 6 shows appropriate chromatographic peaks for the determination of fluoride, chloride, nitrite, hydrogenphosphate and sulphate. With the assistance of block B appropriate standard additions were calculated. The quantitative analysis was successful under the predicted conditions and the determined concentrations were 0.66 mg/l for fluoride, 20.9 mg/l for chloride, 0.50 mg/l for hydrogenphosphate and 6.74 mg/l for sulphate.

Determination of nitrate with conductivity detection is possible but not simultaneously with hydrogenphosphate. Detection of nitrate in a more appropriate detector output range requires the switching of the detector output range between the two anions, which results in an unstable baseline, making the successful determination of hydrogenphosphate impossible. The use of UV detection for the determination of nitrate is a very economical solution. Nitrate can be determined at the same time as bromide, for

which UV detection represents the only possibility (Figs. 6 and 7).

In the accordance with the predictions of block B, for the determination of nitrate in the detector output range 0.005 absorbance and with the calibration graph method, calibration solutions were prepared in the concentration range 2.4–15.0 mg/l. Bromide was determined in the same detector output range with the method of standard additions. The quantitative analysis was successful for both anions; the results were 6.99 and 0.20 mg/l.

With the combination of both detectors all seven anions were successfully determined. With the use of the improved program the planning of quantitative analysis was more rapid and easier.

4. Conclusions

The improvement of the computer program extends its usability to the spectrophotometric detector and allows the selection of the most appropriate detector for many different water samples. This new program covers different real situations more completely and more successfully.

5. References

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