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Expert system for the ion chromatographic determination of alkali and alkaline earth metals in mineral waters

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Abstract

The main limiting factors (the highest concentration that may be injected, the lowest concentrations that can be determined, attainable quality of results and limitations arising from the interfering effects of ions in much higher concentrations) that could prevent the successful suppressed ion chromatographic determination of lithium, sodium, ammonium, potassium, magnesium, calcium and strontium in any particular mineral water were obtained experimentally and organized into three databases supporting the operation of an expert system. The expert system permits the planning of appropriate dilutions, the prediction of suitable detector output ranges, the planning of the appropriate standard additions or concentrations of calibration solutions necessary for the successful quantitative analysis and predicts interferences for the determination of individual ions in particular real samples. The predictions of the expert system were checked experimentally on two different natural samples. All the predictions were realistic and, although very simple calculations were used by the expert system, appropriate distinction between different extents of interferences was achieved. The described expert system works well and offers significant support to the planning of the analysis of different natural mineral waters.

1. Introduction

In contrast to the suppressed ion chromatographic determination of anions, there are relatively few applications for the determination of both alkali and alkaline earth cations in natural waters. However, the development of a cation self-regenerating suppressor [1] and a novel Dionex IonPac CS12 column which permits the simultaneous isocratic determination of lithium, sodium, ammonium, potassium, magnesium, calcium and strontium and shows better sodium–ammonium and ammonium–potassium selectivity than previous columns [2,3] promises good

opportunities also for more diverse and more complicated samples such as mineral waters. Mineral waters from central Europe [4] represent an extensive group of natural samples with very different total concentrations of dissolved solids (at least 1 g/l) and different concentrations and concentration proportions between individual ions. Sodium, potassium, magnesium and calcium can be present at concentrations up to several grams per litre. In an individual mineral water, one or a few of these cations usually predominate significantly, the others being present at concentrations from a few to several orders of magnitude lower. In the analysis of such samples with any analytical technique, the question of how the constituents present at

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higher concentrations affect the determination of those present at lower concentrations plays a very important role and determines the extent to which a particular mineral water can be analysed with a selected analytical method.

Our previous computer programs [5,6], which were intended to facilitate the determination of anions in different natural waters, can also be helpful in the planning of the determination of cations in mineral waters, provided that an adequate experimentally based database for cations is first added. However, in these procedures each ion is considered as being the only one in the solution, and the answer to the question of the extent to which a particular mineral water can be analysed using suppressed ion chromatography cannot be given.

The aim of this work was to establish the limiting factors that could prevent the successful determination of all seven cations (lithium, sodium, ammonium, potassium, magnesium, calcium and strontium) in natural mineral waters and to develop the structure of an expert system that would consider these limiting factors in the planning of the most appropriate dilutions and other experimental conditions and that would be able to predict the extent to which any particular mineral water can be successfully analysed using suppressed ion chromatography.

2. Experimental

2.1. Apparatus and experimental conditions

The Dionex (Sunnyvale, CA, USA) Model 4000i ion chromatographic apparatus consisted of an IonPac CG12 guard column and IonPac CS12 separation column (diameter of macroporous particles 8.0 μm , ethylvinylbenzene cross-linked with 55% divinylbenzene, carboxylic functionality, capacity 2800 $\mu\text{equiv.}$ per column), a cation self-regenerating suppressor (4 mm) and a Dionex conductimetric detector II (CMD). The injection volume was 25 μl and the eluent flow-rate was 1.0 ml/min. A spectra-Physics (San Jose, CA, USA) SP 4290 integrator was used.

2.2. Reagents and procedures

Stock standard solutions of cations were prepared at a concentration of 1 g/l from analytical-reagent grade chemicals using deionized water obtained from a Milli-Q water-purification system (Millipore, Bedford, MA, USA). A stock standard solution of the eluent with a concentration of 1 mol/l was prepared from 98% methanesulphonic acid purchased from Merck-Schuchardt (Hohenbrunn bei München, Germany) and an eluent containing 20 mmol/l methanesulphonic acid was prepared daily from it.

Hydrochloric acid (Titrisol) of concentration 100 mmol/l was purchased from Merck (Darmstadt, Germany) and was used for the neutralization of hydrogencarbonate in mineral waters.

2.3. Basic experiment

We intended to build up an experimentally based database that would enable one to estimate how, in different mineral waters, the predominant ions (sodium, potassium, calcium or magnesium) would affect the determination of other cations. In order to cover the many different concentration proportions with the smallest possible number of experimental steps, the experiment was divided into two separate parts. The results of the first part simulate chromatographic peaks that could interfere with the chromatographic peaks of analyte ions (simulated in the second part of the experiment).

Detector output ranges between 0.1 and 10 μS were used in the first part of the experiment. The solutions of potentially interfering cations (sodium, potassium, magnesium and calcium) were injected not only with the detector output range suitable for the determination of individual cations but also at lower detector output ranges. About 380 experiments were carried out; the concentration ranges of individual ions are summarized in Table 1 (experiment A).

The second experiment covered all six useful detector output ranges between 0.03 and 10 μS . For each detector output range a solution with

Table 1
Concentration ranges of ions in individual experiments

Ion	<i>c</i> (mg/l)			
	Experiment A	Experiment B	Experiment C	Experiment D
Li ⁺	–	0.0054–1.17	1.00–9.40	4.00–39.0
Na ⁺	0.018–9.20	0.011–3.73	4.00–32.0	16.0–142
NH ₄ ⁺	–	0.016–7.50	6.00–24.0	10.0–150
K ⁺	0.053–15.6	0.033–10.6	12.0–82.0	10.0–360
Mg ²⁺	0.013–8.89	0.072–2.50	2.00–20.0	8.00–106
Ca ²⁺	0.030–15.9	0.006–8.74	2.00–16.0	5.00–180
Sr ²⁺	–	0.069–22.9	17.0–136	60.0–620

appropriate concentrations of all seven cations was prepared. The concentration ranges of individual ions covered with these experiments are summarized in Table 1 (experiment B).

2.4. Linearity for lower concentrations of cations

Some preliminary investigations [7] of the repeatability of the measurements of peak areas and peak heights of all seven cations at detector output ranges from 0.03 to 10 μ S showed higher relative standard deviations for the results obtained at the lowest two detector output ranges. Experiments carried out previously with anions showed that only five out of seven anions can be determined at a detector output range of 0.1 μ S and only two at a detector output range of 0.03 μ S. Therefore, the existence of the linear relationship between peak area or peak height and the concentrations of all seven cations had to be checked for the two lowest detector output ranges. Each experiment was carried out with at least eight solutions with different concentrations and each solution was injected at least twice. The concentration ranges of individual ions are summarized in Table 1 (experiment C was performed at a detector output range of 0.03 μ S and experiment D at a detector output range of 0.1 μ S). Although some correlation factors (*r*) were not extremely high (between 0.9541 and 0.9982

for a detector output range of 0.03 μ S and between 0.9866 and 0.9996 for 0.1 μ S), linear relationships between peak area or peak height and concentration were realized in all instances (in contrast to the experience with anions).

3. Results and discussion

3.1. Limiting factors and databases

There are mostly four types of limiting factors that determine the extent to which a particular mineral water can be successfully analysed: the highest concentration that can be injected, the lowest concentrations that can be determined, the expected quality of results and limitations arising from the interfering effects of ions in much higher concentrations. Limiting factors and the data necessary for the planning of quantitative analyses are collected in the database QUANTDET. The databases INTERFER and SPECIALC are useful for the estimation of interfering effects.

The database QUANTDET contains six different parameters. Following the producer's recommendation not to inject more than 10 nmol of any one analyte [8], the upper concentration limits (*c*_{max}) for all seven ions were calculated (Table 2). Other parameters given in Table 2 are the highest concentrations (*c*_{maxDOR}) that can

Table 2

Main limiting factors for the planning of quantitative analysis of mineral waters: maximum concentrations that may be injected (c_{\max}), the highest concentrations ($c_{\max\text{DOR}}$) for individual DOR (μS), the lowest concentrations that were successfully injected (c_{\min}) and the limits of detection (LOD) (all concentrations are in mg/l)

Parameter	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
c_{\max}	2.78	9.20	7.22	15.6	9.72	16.0	35.1
c_{\min}	0.0010	0.0040	0.0060	0.0120	0.0020	0.0020	0.01
LOD	0.0005	0.0047	0.0052	0.0130	0.0041	0.0021	0.01

DOR (μS)	$c_{\max\text{DOR}}$						
10	4.23 ^a	12.5 ^a	24.3 ^a	35.0 ^a	8.67	30.5 ^a	79.3 ^a
3	1.26	4.16	6.02	11.0	2.65	8.80	23.2
1	0.43	2.35	2.30	3.72	0.73	2.84	7.24
0.3	0.14	0.38	0.48	1.15	0.24	0.81	2.26
0.1	0.039	0.142	0.17	0.36	0.106	0.18	0.62
0.03	0.0094	0.032	0.030	0.082	0.020	0.016	0.136

^a Only theoretically (higher than c_{\max}).

be successfully detected in individual detector output ranges (DOR), the lowest concentrations that were successfully injected (c_{\min}) and limits of detection (LOD), calculated as proposed in the statistical literature [9], from standard errors of the estimate ($s_{y/x}$) and from the slopes of regression lines obtained on the lowest detector output range (0.03 μS). These data are essential for the planning of appropriate dilutions and for the estimation of their effects on the possibility of the determination of ions at lower concentrations, and they offer the possibility of the prediction of detector output ranges and of the planning of the appropriate standard additions or concentrations of calibration solutions necessary for successful quantitative analysis. The data on the relative standard deviations for the repeated measurement of peak area (RSD_{area}) and peak heights (RSD_{height}) [7] can serve to give an approximate orientation about the quality of results that can be expected for each individual ion in each particular case.

The database INTERFER contains ten different parameters:

$t(\text{begin})$ = time at which the chromatographic peak of the analyte ion starts;

$t(\text{rt})$ = retention time of the chromatographic peak of the analyte ion;

$t(\text{end})$ = time at which the chromatographic peak of the analyte ion ends;

$c\text{-interf}$ = concentration of potentially interfering ion;

$t(0)$ = time at which potentially interfering chromatographic peak begins;

$t\tau(0)$ = time at which potentially interfering chromatographic peak ends;

$t\tau(1)$ = time at which the right edge of potentially interfering chromatographic peak reaches 2.35% of total scale (PTS);

$t\tau(2)$ = time at which the right edge of potentially interfering chromatographic peak reaches 10% of total scale (PTS);

$t\tau(3)$ = time at which the right edge of potentially interfering chromatographic peak reaches 50% of total scale (PTS);

$t\tau(4)$ = time of the last point at which potentially interfering chromatographic peak extends over 100% of total scale.

This database contains about 1000 data. The essential parameters describing the chromatographic peak of the analyte ion and the interfering chromatographic peak are represented in

Fig. 1. Five additional parameters can be calculated:

PTS(begin) = percentage of total scale at which the analyte chromatographic peak begins;

PTS(rt) = percentage of total scale at which the analyte chromatographic peak appears;

PTS(end) = percentage of total scale at which the analyte chromatographic peak ends;

NOVERLAP = percentage of peak width of the analyte ion that is not overlapped with the chromatographic peak of the interfering ion;

RTNOVERL = percentage of peak width be-

tween the end of the chromatographic peak of the interfering ion and the retention time of the chromatographic peak of the analyte ion.

The relationships for their calculation are as follows:

$$PTS(x) = PTS(j) - \frac{[PTS(j) - PTS(j-1)][t(x) - tr(j)]}{tr(j-1) - tr(j)} \quad (1)$$

$j = 0, 1, 2, 3, 4$; (a) $x = \text{begin}$, $PTS(\text{begin}) = PTS(x)$; (b) $x = \text{rt}$, $PTS(\text{rt}) = PTS(x) + PTS$,

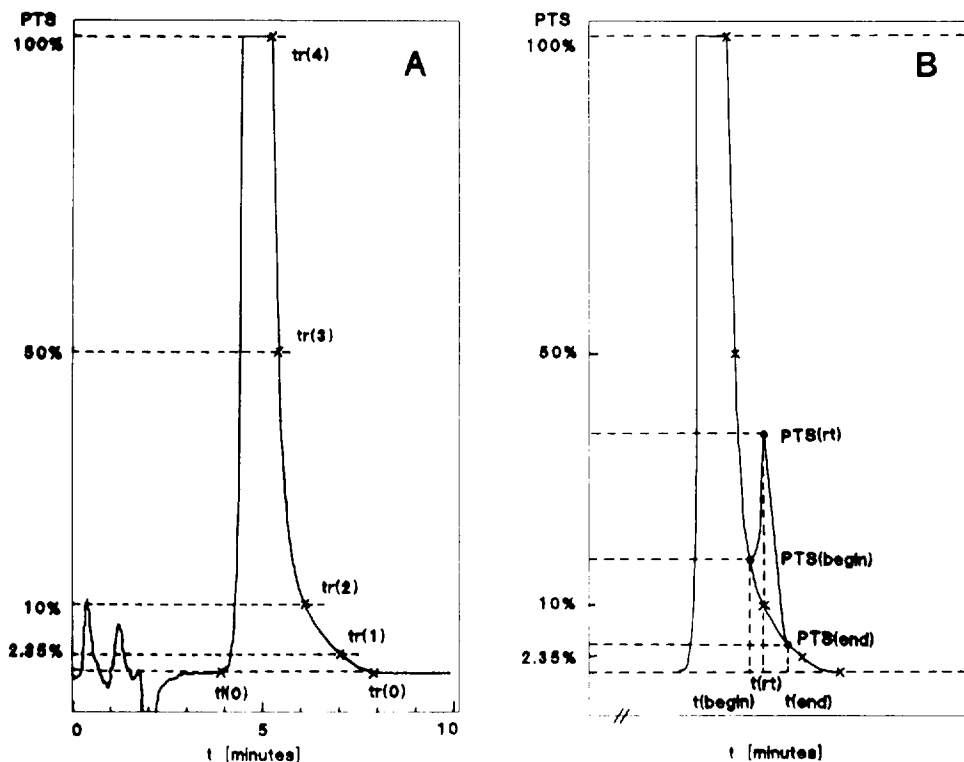


Fig. 1. Graphical representation of the main data collected in the database INTERFER that permit the calculation of the parameters PTS(begin), PTS(rt), PTS(end), NOVERLAP and RTNOVERL for the distinction between different extents of interference between ions. PTS = percentage of total scale; $t(0)$ = time at which interfering chromatographic peak begins; $tr(0)$ = time at which interfering chromatographic peak ends; $tr(1)$ = time at which the right edge of the chromatographic peak reaches 2.35% of the total scale (PTS); $tr(2)$ = time at which the right edge of the chromatographic peak reaches 10% of the total scale (PTS); $tr(3)$ = time at which the right edge of the chromatographic peak reaches 50% of the total scale (PTS); $tr(4)$ = time at the last point at which the chromatographic peak extends over 100% of the total scale; $t(\text{begin})$ = time at which the analyte chromatographic peak starts; $t(\text{rt})$ = retention time of the analyte chromatographic peak; $t(\text{end})$ = time at which the analyte chromatographic peak ends; $PTS(\text{rt})$ = percentage of total scale at which the chromatographic peak appears; $PTS(\text{begin})$ and $PTS(\text{end})$ = percentage of total scale at which the chromatographic peak begins or ends.

PTS = 100 c/c_{\max} DOR, c = concentration of ion in injected sample; (c) x = end, PTS(end) = PTS(x).

$$\text{NOVERLAP} = 100 \cdot \frac{t(\text{end}) - tr(0)}{t(\text{end}) - t(\text{begin})} \quad (2)$$

$$\text{RTNOVERL} = 100 \cdot \frac{t(rt) - tr(0)}{t(\text{end}) - t(\text{begin})} \quad (3)$$

These five parameters were introduced in order to permit the simple distinction between different extents of overlapping between an interfering ion and the ion of interest in any real sample. A related algorithm is described later (Figs. 5 and 6), but in order to facilitate understanding, the roles of individual parameters are explained here. In each particular case, $t(\text{begin})$ of the analyte ion is selected from the database on the basis of a previously predicted DOR suitable for the determination of this cation. The end of the potentially interfering chromatographic peak $tr(0)$ relating to c -interf that is the nearest to the concentration expected in the sample is also selected from the database. The comparison of these two parameters [$t(\text{begin})$ and $tr(0)$] shows if there is any interference

between the two chromatographic peaks, otherwise an interval for the switching of the detector output ranges can be given. The comparison of $t(\text{end})$ of the analyte chromatographic peak and $tr(0)$ shows if the peak width of the analyte ion at the baseline partially or completely overlaps with the interfering ion. If the former is true, parameter NOVERLAP (Eq. 2), describing the extent of interference, can be calculated. The comparison of $t(rt)$ and $tr(0)$ shows if an interfering ion affects the measurement of the peak height of the analyte ion. If not, then calculation of RTNOVERL (Eq. 3) gives the percentage of the peak width of the analyte ion between the end of the interfering peak and the retention time of the determining ion. Calculation of PTS(begin), PTS(rt) and PTS(end) ensures additional insight into the extent of interfering effects. The largest extent can be expected if PTS(begin) exceeds PTS(rt). In this instance determining ion cannot even be observed and overlap with the interfering ion is complete. Appropriate data for the calculation of these parameters (Eq. 1) are selected from the database: the first time that it is lower and the first time that it is higher [$tr(j)$ and $tr(j-1)$]; j =

Table 3
Database SPECIALC

Conditions	Parameter	DOR (μ S)					
		0.03	0.1	0.3	1	3	
A ^a	PTS(begin) (%)	7.75	–	–	–	–	
	NOVERLAP (%)	68.2	–	–	–	–	
	RTNOVERL (%)	15.2	–	–	–	–	
B ^b	PTS(end) (%)	2.35	6.18	21.7	(13.2) ^c	–	1.42
	NOVERLAP (%)	99.0	88.3	83.6	(82.1) ^c	–	91.5
	RTNOVERL (%)	47.5	41.1	40.3	(38.9) ^c	–	50.8
C ^d	PTS(begin) (%)	69.7	(27.1) ^c	1.48	–	–	–
	PTS(end) (%)	15.1	–	–	–	–	–
	NOVERLAP (%)	–	(58.8) ^c	86.6	–	–	–
	RTNOVERL (%)	–	–	33.0	–	–	–

^a $K^+ \rightarrow Ca^{2+}$; c -interf = 15.6 mg/l.

^b $Mg^{2+} \rightarrow K^+$; c -interf = 8.89 mg/l.

^c c -interf = 7.46 mg/l.

^d $Mg^{2+} \rightarrow Sr^{2+}$; c -interf = 8.89 mg/l.

^e c -interf = 7.46 mg/l.

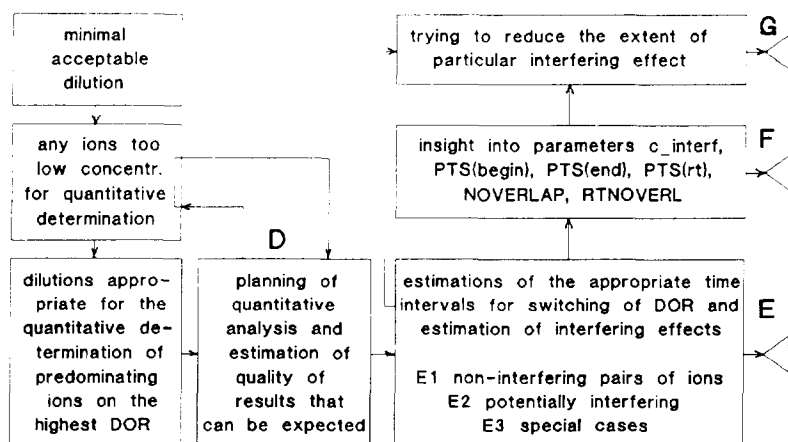


Fig. 2. Structure of the expert system and the main functions of individual blocks.

0,1,2,3,4] than $t(\text{begin})$ or $t(\text{rt})$ or $t(\text{end})$ are used.

Each of the four potentially interfering ions (sodium, potassium, magnesium and calcium) most significantly interferes with ions that follow immediately, e.g., sodium interferes with ammonium, potassium with magnesium, magnesium with calcium and calcium with strontium. The

interferences that have a very limited extent (only a few $c\text{-interf}$ and only a few DOR) are covered as special cases. This significantly reduced the size of the database INTERFER. A much smaller database (SPECIALC) with already calculated parameters $\text{PTS}(\text{begin})$, $\text{PTS}(\text{end})$, NOVERLAP and RTNOVERL was introduced. It is summarized in Table 3.

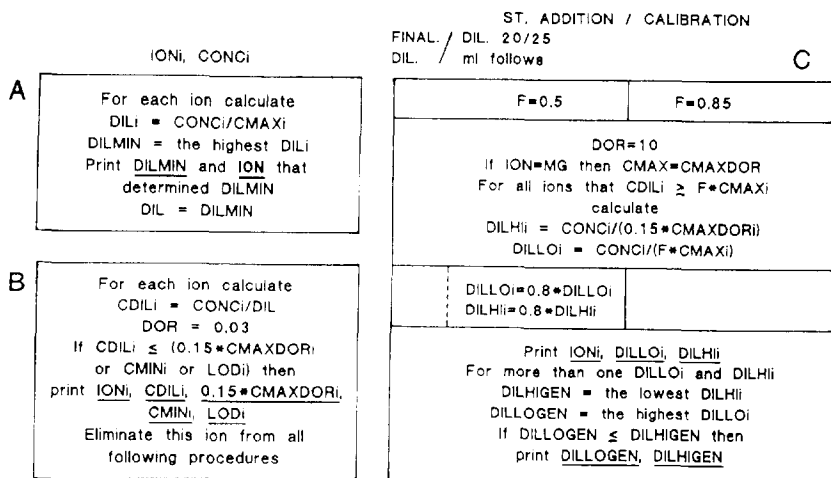


Fig. 3. Main operations of blocks A, B and C. The input data for block A are approximate concentrations (CONC_i) of individual ions (ION_i). For the operation of block C, selection between method of standard additions and method of calibration function (ST. ADDITION/CALIBRATION) has to be done first. If the first option was selected there is also the distinction between the case in which dilution means the final dilution (FINAL. DIL) and the case in which further dilution connected with standard additions follows (DIL. 20/25 ml follows; 20 ml of already diluted sample introduced into a 25-ml volumetric flask). All other data necessary for the operation of these three blocks are obtained from the database QUANTDET.

3.2. Expert system

Operations relating to experimentally obtained data collected in the three databases QUANTDET, INTERFER and SPECIALC were already briefly considered above, but the complete structure of the expert system and the main functions of individual blocks are represented in Fig. 2. The detailed structure and operation of the seven blocks are represented in Figs. 3-6. Input data are represented at the top of an individual block and other data are selected from the appropriate databases. The database necessary for the operation of an individual block is specified below each figure. In the structure of

DIL		D
ST. ADDITION / CALIBRATION		
FINAL. / DIL. 20/25 ml follows		
F=55	F=85	
DIL=1.25*DIL		
go to B and return For all remaining ions print <u>ION_i</u> , <u>CDIL_i</u>		
For ions for which DILLO, DILHI calculated DOR=10 For $C_i=CDIL_i$ calculate PTS_i For $ION\#MG$ calculate PTS_i also for $C_i=C_{MAX_i}$		
For all other ions find all DOR_i for which $15 \leq PTS_i \leq F$		
For each ion select higher DOR	For each ion select DOR with PTS nearer to 50	
Print <u>DOR_i</u> , <u>PTS_i</u> , <u>PTS_i</u> for <u>C_{MAX_i}</u>		
For DOR=10 and $ION\#MG$ $C_{MAXDOR}=C_{MAX}$		
Calculate MIX_i $MIX_i=C_{MAXDOR_i}-CDIL_i$ Print <u>MIX_i</u>	$C1_i=0.15*C_{MAXDOR_i}$ $CN_i=C_{MAXDOR_i}$ Print <u>C1_i</u> , <u>CN_i</u>	
Print <u>RSDAREA_i</u> , <u>RSDHEIGH_i</u>		

Fig. 4. Main operations of block D. Dilution has to be selected first. Other data are introduced from the database QUANTDET. The relationship $PTS = 100c/c_{maxDOR}$ is used for the calculation of the percentage of total scale at which the chromatographic peaks of individual ions appear using selected detector output ranges; c means the concentration of an ion in the injected sample.

each block, output data are underlined. In order to allow an understanding of the operation of the expert system, the meanings of some additional variables are given as follows:

c_1 = minimal concentration of calibration solution (mg/l),

$cdil$ = concentration of ion after dilution (mg/l);

cn = maximum concentration of calibration solution (mg/l);

$conc$ = approximate concentration of the ion in the sample (mg/l);

DIL = dilution;

DILHI = highest possible dilution for determination of ion on DOR = 10;

DILHIGEN = highest general dilution appropriate for all ions that have to be determined on DOR = 10;

DILLO = lowest possible dilution for determination of ion on DOR = 10;

DILLOGEN = lowest general dilution appropriate for all ions that have to be determined on DOR = 10;

DILMAX = maximum acceptable dilution for determination of an ion;

F = factor that determines the maximum concentration that can be successfully determined in a selected detector output range;

MINDIL = minimum dilution that does not cause overloading of the column;

MIX = maximum possible increase in concentration (mg/l) for the determination of an ion by the method of standard additions;

SWITCHIN = time interval (minutes) for switching of DOR between two ions.

The main function of block A is to find the ion that most significantly exceeds the maximum allowed concentration (c_{max}) and to calculate minimum dilution (DILMIN) that appropriately decreases its concentration. Block B offers the possibility of checking whether the concentration of any ion after dilution became too low for determination and excludes such an ion from all further procedures. Dilutions (DILLO, DILHI) appropriate for the determination of the predominant ions on the highest DOR are predicted using block C. If there are more ions that have to be determined on DOR = 10 μ S, block C also

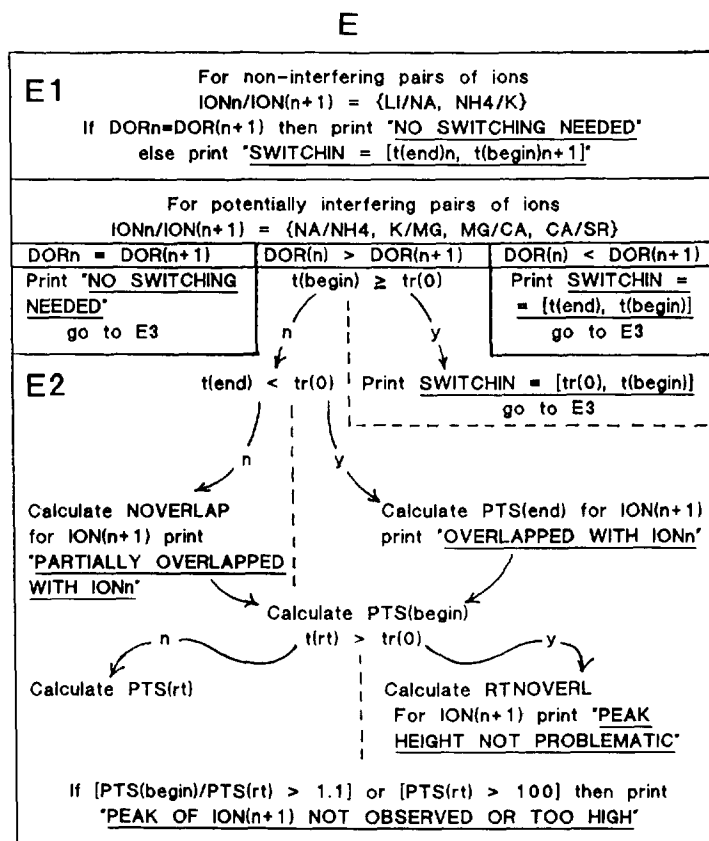


Fig. 5. Main operations of the first two parts (E1, E2) of block E. The database INTERFER is used. Eqs. 1-3 for the calculation of the parameters $\text{PTS}(\text{begin})$, $\text{PTS}(\text{rt})$, $\text{PTS}(\text{end})$, NOVERLAP and RTNOVERL were described in Section 3.1.

tries to find general dilutions (DILLOGEN, DILHIGEN) appropriate for all of them. There is a distinction between the method of calibration function and the method of standard additions. For the method of standard additions the specification of dilution means final dilution or if there is another step in which the concentration of ions is further reduced [20 ml of diluted sample introduced into a volumetric flask (25 ml), standard additions for individual ions added and then diluted with deionized water to 25 ml]. On the basis of the suggestions about suitable dilutions, the most appropriate dilution (DIL) can be selected and introduced into block D. This block finds the most suitable detector output ranges for the determination of individual ions, suggests appropriate standard additions

(MIX) or concentrations of calibration solutions (c_1, c_n), and reports the relative standard deviations for the measurement of areas or heights of chromatographic peaks of individual ions in selected detector output ranges (RSD_{area} , $\text{RSD}_{\text{height}}$). Block E permits the prediction of time intervals useful for switching between different detector output ranges during elution and estimates if there are any interfering effects caused by large differences in concentrations of individual ions. It classifies the interferences of different extents. Block F offers an insight into parameters that were calculated in the previous block and that permitted classification. The main function of block G is to check if increased dilution reduces a particular interfering effect.

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For special cases IONn/ION(n+1) = (K/CA, MG/K, MG/SR)

If CDIL(K) > 9.5 and DOR(CA) = 0.03 then read SPECIALC
If [CDIL(MG) > 7.46 and DOR(K) ≠ 0.3] or [CDIL(MG) > 2.2 and
DOR(K) = 0.3] then read SPECIALC
If CDIL(MG) > 2.2 and DOR(SR) = 0.03 then read SPECIALC

For IONn/ION(n+1) ignore PTS(end)

If PTS(end) > 0 then for ION(n+1) print
'OVERLAPPED WITH IONn'
If NOVERLAP > 0 then for ION(n+1) print
'PARTIALLY OVERLAPPED WITH IONn'
If RTNOVERL > 0 then for ION(n+1) print
'PEAK HEIGHT NOT PROBLEMATIC'
E3

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F IONn/ION(n+1)

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Print parameters C_INTERF, PTS(begin), PTS(rt), PTS(end),
NOVERLAP, RTOVERL previously calculated in bloc E

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G IONn/ION(n+1)

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DOR=0.03
DIL = CONC/(0.15*CMAXDOR)
MAXDIL=DIL
If method of standard additions previously selected and dilution
20/25 ml follows then MAXDIL = 0.8*DIL
Print MAXDIL
Repeat procedures E2, E3, optionally F and return
Print SWITCHIN or description of the extent of overlapping

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Fig. 6. Main operations of blocks E3, F and G. Blocks F and G are optional and pairs of ions in which one is interested have to be defined first. The database SPECIALC permits the operation of block E3. Block F utilizes data calculated in block E. Data for the operation of block G are obtained from the database QUANTDET.

3.3. Real mineral water samples

Two real samples, mineral water with the trade-name Petanjski Vrelec and mineral water from the bore-hole V-P (both from the health resort Radenska, Radenci, Slovenia), with different compositions and different total mineralization were selected, in order to illustrate the operation of the described expert system. We tried to cover all functions of the expert system so at the beginning of block C the method of calibration function was selected for Petanjski Vrelec and the method of standard additions (with dilution from 20 to 25 ml) for sample V-P.

Approximate concentrations of individual ions (input data) and predictions for Petanjski Vrelec are summarized in Table 4. Table 5 gives the data for sample V-P. There are significant differences between the two predictions. In the former instance, sodium determines the necessary minimum dilution (DILMIN), in the latter calcium. DILMIN for sample V-P is more than ten times lower than DILMIN for Petanjski Vrelec. After minimum dilution the concentrations of all ions in sample V-P are high enough for determination. At the unavoidable minimum dilution strontium cannot be detected in Petanjski Vrelec mineral water.

Table 4

Predictions for natural mineral water Petanjski Vrelec obtained by the expert system

(A) DILMIN = 70		Ion = Na				
(B) Concentration of Sr too low						
cdil(Sr) = 0.014 mg/l		0.15cmax = 0.020 mg/l				
cmin = 0.017 mg/l		LOD = 0.016 mg/l				
(C) Dilutions appropriate for quantitative determination of predominant ions at DOR 10 μ S						
Ion = Na		DILLO = 83		DILHI = 345		
(D) Dilution DIL = 200						
Parameter	Li	Na	NH ₄	K	Mg	Ca
cdil (mg/l)	0.002	3.23	0.012	0.33	0.25	0.78
DOR (μ S)	0.03	10	0.03	0.3	1	1
PTS (%)	21.3	25.8	40.0	28.7	34.2	27.5
PTS (cmax) (%)	–	73.6	–	–	–	–
c1 (mg/l)	0.0014	1.38	0.005	0.17	0.11	0.43
cn (mg/l)	0.0094	9.20	0.03	1.15	0.73	2.84
RSDarea (%)	12.1	0.6	11.3	4.8	1.1	1.1
RSDheigh (%)	4.6	0.4	10.5	4.7	0.5	0.7
(E)						
SWITCHIN (min)	(3.55,		(5.20,	(6.70,		No switching
Ion	3.67)		5.36)	6.70)		needed
NH ₄	(Lower c-interf)		(Higher c-interf)			
	Partially overlapped		Overlapped with Na,			
	with NA		peak of NH ₄ not			
			observed or too high			
(F) ION = NH ₄						
c-interf	PTS(begin)	PTS(rt)	PTS(end)	NOVERLAP	RTOVERL	
1.80	36.7	45.0	–	25.0	–	
3.30	108	86.8	7.7	–	–	

The main input data for the operation of the expert system were approximate concentrations of individual ions 0.41 mg/l for lithium, 646 mg/l for sodium, 2.30 mg/l for ammonium, 65.0 mg/l for potassium, 49.5 mg/l for magnesium, 155 mg/l for calcium and 1.00 mg/l for strontium.

Dilutions appropriate for the determination of sodium in Petanjski Vrelec water in the detector output range 10 μ S extend from 83- to 345-fold and for further predictions we decided to use a 200-fold dilution (input data for block D). In the mineral water V-P two ions, calcium and magnesium, have to be determined at DOR = 10 μ S. General dilutions appropriate for both of them are between 8.9- and 16-fold; we selected a tenfold dilution for further work. Only for the determination of lithium predicted in block D was the detector output range the same (0.03 μ S) for both samples; for all others it differed.

Block E reports time intervals for switching of the detector output ranges between lithium and sodium, between ammonium and potassium and between potassium and magnesium for Petanjski Vrelec mineral water and between lithium and sodium and between potassium and magnesium for sample V-P. In both instances no switching is needed between magnesium and calcium and for sample V-P also between ammonium and potassium. Block E estimates that ammonium in sample V-P partially overlaps with sodium. The greatest interference with calcium is observed for strontium and there is also interference with

Table 5
Predictions for natural mineral water V-P obtained by expert system

(A)	DILMIN = 5.6		Ion = Ca					
(C)	Dilutions appropriate for quantitative determination of predominant ions at DOR 10 μ S							
	Ion = Mg	DILLO = 6.2		DILHI = 21				
	Ion = Ca	DILLO = 8.9		DILHI = 16				
	DILLOGEN = 8.9		DILHIGEN = 16					
(D)	Dilution DIL = 10							
	Parameter	Li	Na	NH ₄	K	Mg	Ca	Sr
	cdil (mg/l)	0.0048	0.88	0.04	0.16	2.69	7.11	0.036
	DOR (μ S)	0.03	3	0.1	0.1	10	10	0.03
	PTS (%)	52.1	21.2	23.5	40.4	31.0	23.3	26.5
	PTS (cmax) (%)	-	-	-	-	-	51.8	-
	MIX (mg/l)	0.0046	3.28	0.13	0.20	5.98	8.89	0.100
	RSDarea (%)	12.1	1.2	11.0	4.6	0.8	0.8	9.4
	RSDheigh (%)	4.6	1.0	6.7	2.7	0.4	0.5	7.1
(E)	SWITCHIN (min)	(3.55, 3.67)		No switching needed	(6.58, 6.68)	No switching needed		
	Ion	(Lower c interf)			(Higher c-interf)			
	NH ₄	Partially overlapped with NA			Partially overlapped with NA			
	Sr	Overlapped with Ca, peak of Sr not observed or too high			Overlapped with Ca, peak of Sr not observed or too high			
		Overlapped with Mg			Overlapped with Mg			
(G)	Sr	Overlapped with Ca, peak of SR not observed or too high			Overlapped with Ca, peak of Sr not observed or too high			
	MAXDIL = 17.6							

The main input data for the operation of the expert system were approximate concentrations of individual ions 0.06 mg/l for lithium, 11.0 mg/l for sodium, 0.5 mg/l for ammonium, 2.0 mg/l for potassium, 33.6 mg/l for magnesium, 88.9 mg/l for calcium and 0.45 mg/l for strontium.

magnesium (one of the few special cases from the database SPECIALC).

In order to estimate the possibility of decreasing these interfering effects, block G was activated. However, although at the maximum dilution acceptable for the determination of strontium, the extent of interference remains the same. Also in mineral water V-P strontium could not be detected, although its concentration is not below the limit of detection as it is in Petanjski Vrelec mineral water.

The estimates of the extent of the interfering effect of sodium on ammonium obtained from

two c-interfer, the closest to the approximate concentration of sodium in diluted Petanjski Vrelec sample (the next higher and the next lower concentration), do not agree. In order to find out which one represents a better approximation of real situation, block F was used. The value c-interfer = 3.30 is very close to cdil = 3.23, so it is more realistic to expect greater interference that would certainly prevent the determination of ammonium.

The predictions for both mineral waters were checked in the experiments under predicted conditions. The chromatograms are shown in

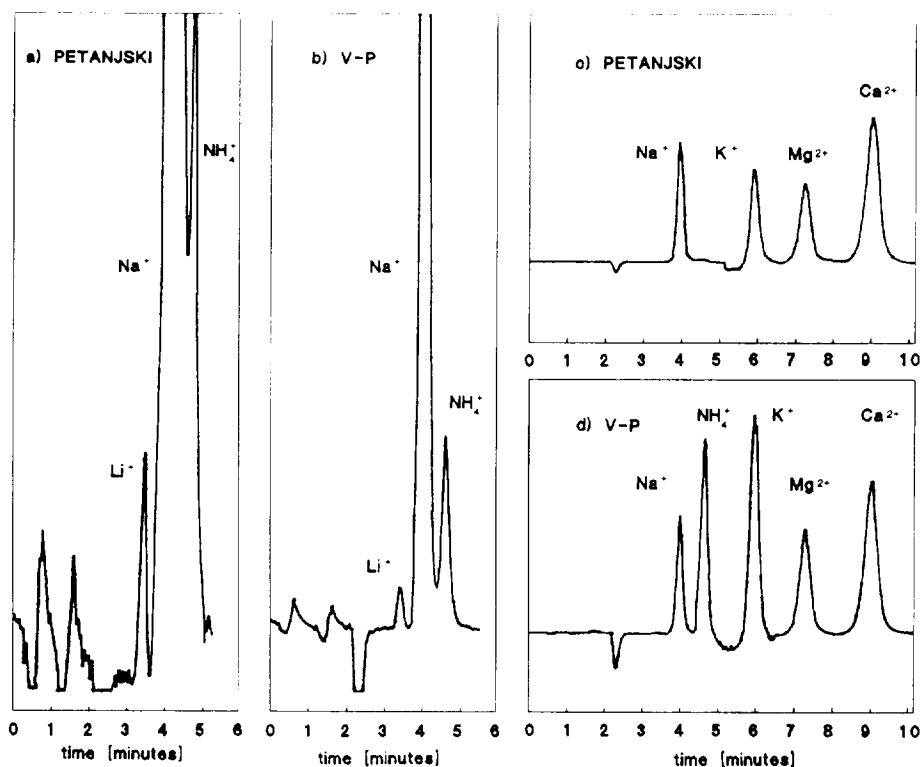


Fig. 7. Chromatograms of two different natural mineral waters obtained under conditions predicted by the expert system. Sample Petanjski Vrelec was diluted 200-fold and sample V-P 10-fold. The eluent was methanesulphonic acid at a concentration of 20 mmol/l. Chromatograms (a) and (b) were obtained with detector output ranges (DOR) 0.03 and 0.1 μS , respectively; in the other two cases DOR was switched during elution in accordance with the predictions summarized in Tables 4 and 5. The sequence was DOR = 10 μS for sodium, 0.3 μS for potassium and 1 μS for magnesium and calcium in (c) and DOR = 3 μS for sodium, 0.1 μS for ammonium and potassium and 10 μS for magnesium and calcium in (d).

Fig. 7. All the predictions were realistic and although very simple calculations were used [parameters PTS(begin), PTS(rt), PTS(end), NOVERLAP, RTNOVERL], appropriate distinctions between different extents of interferences were achieved.

The described expert system works well and offers significant support to the planing of the analysis of different natural mineral waters and prevents wastage of time and efforts to find solutions in situations that are unresolvable under the conditions involved.

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