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Simple recognition of similar samples for the ion-chromatographic determination of the main cations

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Abstract

In order to develop methodology for the simple recognition of samples that are very similar by ion-chromatographic analysis, 116 different Slovenian water samples, of known composition, were considered. Suitable dilutions and appropriate detector output ranges for the ion-chromatographic determination of sodium, magnesium and calcium were predicted. These data were related to data on the chemical composition of each individual water sample, expressed in mequiv.%. A triangular diagram was designed. This is a sort of ion chromatographic map that enables institutions dealing with the periodical checking of numerous different samples to recognize the most similar samples easily and allows for the very fast and efficient transition from traditional to ion chromatographic analysis. The accuracy of the predictions was checked experimentally. © 1997 Elsevier Science B.V.

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1. Introduction

The importance and use of ion chromatography for the analysis of different real samples is increasing all the time. But even now, some groups of more versatile samples e.g. mineral waters are often routinely analyzed by other analytical methods. The reason is the great variety in the composition of such samples.

Mineral waters are an extensive group of natural samples with very different total concentrations of dissolved solids (at least 1 g/l) and different concentrations and proportions of the 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. The use of mineral waters for recreational, therapeutic and other purposes already has a long tradition. Natural aquifers are well researched and new mineral waters sources with completely different compositions are very seldom found. Institutions dealing with the analysis of these natural samples are faced with the problem of periodically checking the quality and composition of this very versatile group of samples, however, the composition of these samples does not change significantly from one sampling to another. This means that the problem is complex but well defined.

For the successful ion-chromatographic analysis of such samples, more planning of the experimental conditions is needed. We have been working on the development of algorithms that facilitate the selection of the appropriate experimental conditions for the ion-chromatographic determination of anions [1,2] and cations [3] in different samples. For

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Table 1
Data on the composition of 116 different Slovenian water samples

	Minimum	Maximum	Average	Median	Number of samples
TDS, mg/l	152	15520	4313	3682	116
Total CO ₂ , mg/l	16	4495	1765	1828	98
[Na ⁺], mg/l	0.3	4960	804.1	500	116
[Ca ²⁺], mg/l	3.9	509	171.8	154.5	116
[Mg ²⁺], mg/l	1	1255	95.3	56.0	116
[K ⁺], mg/l	0.1	520	81.0	50.0	113

TDS=total dissolved solids.

institutions dealing with the periodic checking of the quality or composition of hundreds of different samples, methods that allow prediction for only one sample at a time are not fast enough.

The aim of our work was to develop methodology that could be used to recognize the samples that can be analyzed by ion-chromatography at very similar experimental conditions and to make a type of ion chromatographic map that would enable institutions dealing with the periodic checking of numerous different samples to change quickly and efficiently from traditional methods to ion-chromatographic analysis.

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 an IonPac CS12 separator column, a cation self-regenerating suppressor (4 mm) and a Dionex conductivity detector II

(CMD). The injection volume and the eluent flow-rate were 25 µl and 1 ml/min, respectively. A two-channel ChromJet integrator (Thermo Separation Products, Fremont, CA, USA) was used.

2.2. Reagents and solutions

All solutions were prepared 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 (1 mol/l) was prepared from 98% methanesulphonic acid, which was purchased from Merck-Schuchardt (Hohenbrunn bei Munich, Germany) and an eluent containing 20 mmol/l methanesulphonic acid was prepared daily from it.

2.3. Samples of mineral water

The mineral water samples were ultrasonically degassed (8 min) and injected into the ion chromatography apparatus after appropriate dilution.

Table 2
Predicted dilutions and concentrations of individual cations in real samples after dilution

	Minimum	Maximum	Average	Median	Number of samples
Dilution	1.790	634.3	104.5	63.9	116
<i>After dilution</i>					
[Na ⁺], mg/l	0.055	7.82	6.54	7.82	116
[Ca ²⁺], mg/l	0.011	13.6	5.25	2.63	116
[Mg ²⁺], mg/l	0.0029	8.26	2.31	1.14	116
[K ⁺], mg/l	0.018	3.63	0.827	0.675	113

Table 3

Sequence of detector output ranges that is suitable for the ion-chromatographic analysis of 116 different Slovenian water samples

Detector output range (μS)			Combination	Frequency
Na^+	Mg^{2+}	Ca^{2+}		
0.1	10	10	A	1
0.3	10	10	B	3
3	10	10	C	4
10	10	10	D	43
10	—	0.03	E	1
10	0.0	0.1	F	1
10	3	3	G	12
10	0.1	0.1	I	2
10	0.1	0.3	J	3
10	0.3	0.3	K	1
10	1	1	L	23
10	1	3	M	12
10	3	10	N	9
10	0.3	0.1	O	1

3. Results and discussion

In order to ensure a sufficiently wide and representative group of real samples, 116 water samples from all of the most important Slovenian health resorts and also from other potentially interesting bore holes from different regions were taken into account. These waters can be classified as mineral (64.7%), thermomineral (21.6%), thermal (10.3%) or usual drinking water (3.5%). Their composition is fairly different. The main data are summarized in Table 1. All of these water samples were analyzed using traditional analytical methods.

Methodology for the prediction of appropriate experimental conditions was based on the use of an algorithm and experimentally determined databases and have been described in detail previously [3]. Similar methodology was applied here to the entire group comprising 116 different real samples. Appro-

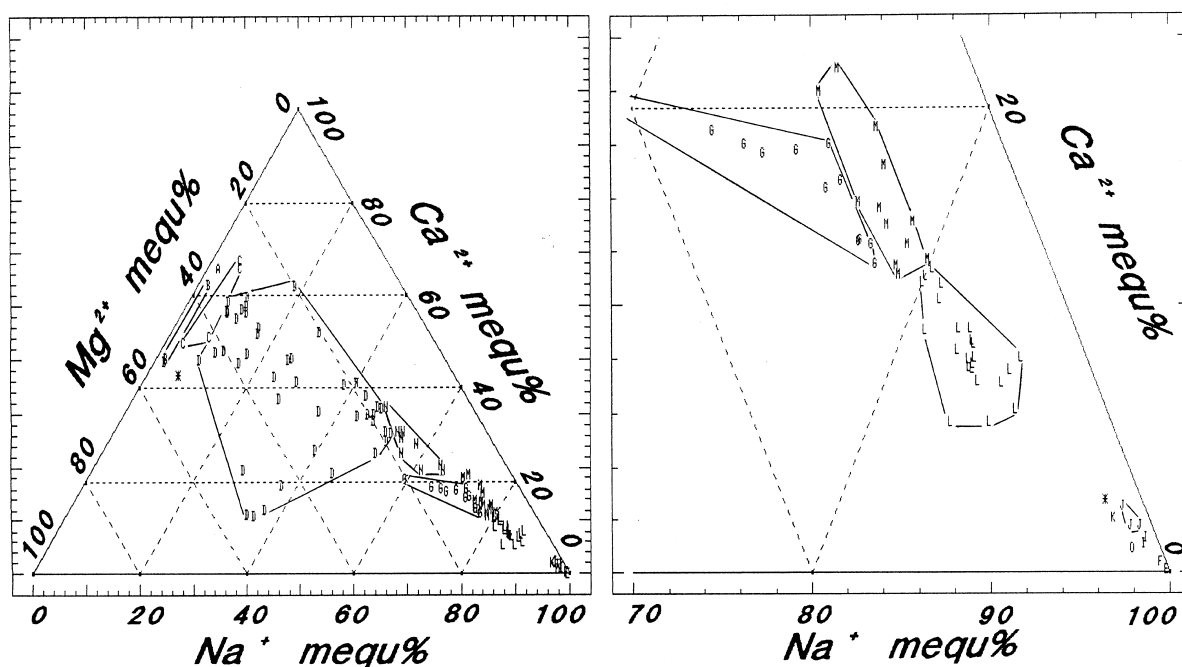


Fig. 1. Ion chromatographic map connecting the cationic composition of 116 Slovenian water samples with the appropriate sequence of detector output ranges, represented by different points and explained in Table 3. On the right-hand side is an enlargement of the right corner of the triangular diagram.

priate dilutions and detector output ranges for the determination of the main cations were predicted. Concentration ranges of individual cations in samples after dilution and the dilutions used are summarized in Table 2. All 116 water samples were then organized into groups according to the detector output ranges that were suitable for the determination of the main three cations, sodium, magnesium and calcium. Only fourteen different combinations of detector output ranges were found. The results are summarized in Table 3. After the classification of all 116 samples into fourteen groups, we have been looking for the parameter representing chemical composition of individual samples and at the same time also showing the similarities for ion chromatographic analysis most precisely. The representation of chemical composition in terms of mequiv.% was selected. Although mequiv.% is not an SI unit, it is unavoidable when comparing the composition of different mineral waters. It is obtained from the ratio between the mequiv. of individual cations and the sum of the mequiv. of all cations present. The chemical composition of each individual water sam-

ple was connected by the prediction of the appropriate sequence of detector output ranges that was suitable for ion chromatographic analysis. For the graphical representation of all of these data, a triangular diagram was selected (Fig. 1). It enables the simultaneous representation of four main items of data. The position of each point in the diagram shows the chemical composition of a sample, but the letter represents the appropriate detector output ranges required for the successful ion chromatographic analysis of these samples (Table 3). Points are spread over almost the whole area of the diagram. This means that the 116 Slovenian water samples were different enough and can serve as a representative model for the vast majority of natural water samples. The triangular diagram is a type of ion chromatographic map that enables one to predict the appropriate experimental conditions required not only for the 116 Slovenian water samples represented here, but also for other similar samples. The predicting ability of the ion chromatographic map was checked for two very different samples. The first sample contained 4.94 mequiv.% of sodium, 42.8

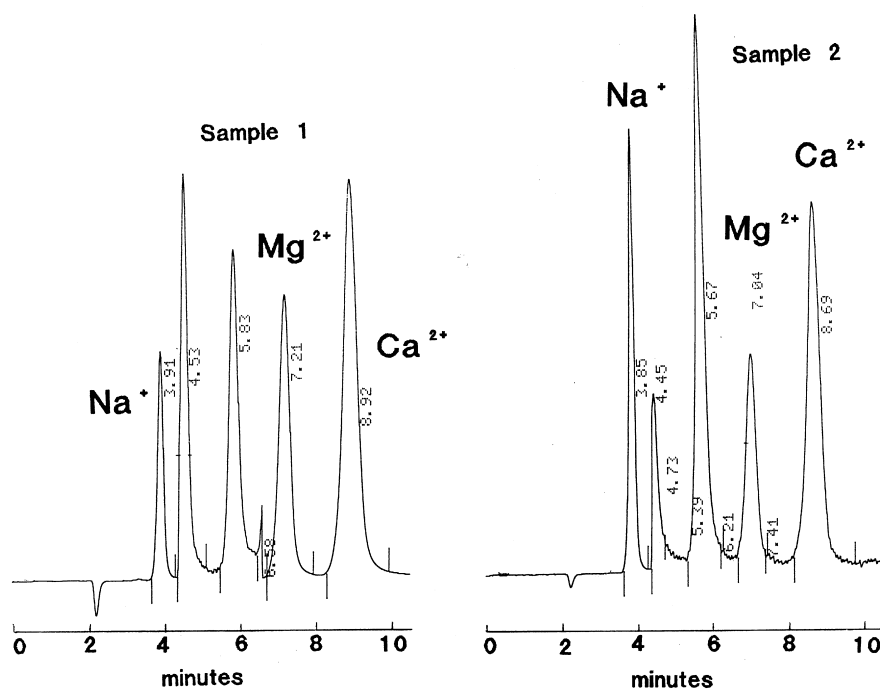


Fig. 2. Chromatograms of two different water samples, recorded under experimental conditions predicted with the assistance of the ion chromatographic map.

mequiv.% of calcium and 51.5 mequiv.% of magnesium. Its composition is represented by an asterisk on the left-hand side of Fig. 1 and the ion chromatographic map suggests a combination of detector output ranges as represented by point C. This means that a detector output range of 3 μS should be used for the determination of sodium and 10 μS is required for the determination of magnesium and calcium. The second sample contained 89.9 mequiv.% of sodium, 3.20 mequiv.% of calcium and 2.00 mequiv.% of magnesium. This sample is also represented by an asterisk, but it is located on the right-hand side of Fig. 1. This asterisk is the closest to point K, which represents the following sequence of detector output ranges: 10 μS for the determination sodium and 0.3 μS for the determination of magnesium and calcium. Both samples were injected into ion chromatography system and chromatograms were recorded under the predicted conditions. The chromatograms obtained are shown in Fig. 2 and they both show that the predictions from the ion-chromatographic map were accurate and directly applicable.

4. Conclusions

Using the proposed methodology, each institution dealing with the analysis of samples can build their own ion-chromatographic map which would enable them to change easily and quickly from traditional methods, e.g. titrimetric and different spectrometric (atomic emission spectroscopy, atomic absorbance spectroscopy), to the ion-chromatographic determination of cations in different samples. Such a map also has the potential to be able to predict conditions for other samples of similar composition.

References

- [1] N. Gros, B. Gorenc, *Chromatographia* 36 (1993) 251.
- [2] N. Gros, B. Gorenc, *J. Chromatogr. A* 668 (1994) 385.
- [3] N. Gros, B. Gorenc, *J. Chromatogr. A* 697 (1995) 31.