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SYSTEM PEAK IN ION CHROMATOGRAPHY

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Abstract. In ion chromatography the equilibrium is disturbed after an injection and then the re-equilibrium process occurs resulting in extraneous peaks (known as system peaks). In the present work the origin of the system peak and the relation between the area of the system peak and the anion concentration of the sample were studied. It was also examined how the fact that the system peak is the largest peak on the chromatogram under certain experimental conditions could be used to determine the ion content of the analysed sample.

The results of the conducted measurements revealed a linear dependence between the area of the system peak and the anion concentration of the sample. It was also proved that the system peak as the largest peak on the chromatogram can be used to lower the detection limit of the total anion concentration of the sample.

Key words: system peak, ion chromatography, total anion concentration, detection limit.

INTRODUCTION

Extraneous peaks (which are not directly related to the injected solutes) are commonly observed in ion-pair [1] and ion exchange chromatography [2–4]. Other names for these peaks as referred to in literature are system peaks, eigenpeaks, injection peaks, pseudo-peaks, ghost peaks, vacancy peaks, induced peaks, etc. The most appropriate name is probably "system peaks" since terms like eigenpeaks have a wrong connotation and there is nothing pseudo- or ghostlike about them either [3]. On a chromatogram, more than one such peak can be seen [3, 5–7]. Two kinds of peaks can be distinguished based on their retention behaviour: peaks with a constant retention time and those with a changeable retention time. The peak examined in the current paper is always the first on the chromatogram and it is eluted at the column void volume. The peak's direction can be either positive or negative. The origin

of the peak has been investigated by various authors [2–4] in different chromatographic systems.

Limiting the choice of the systems by the anion-exchange chromatography, a summary of the hypotheses published so far can be presented. According to these, the origin of the system peak can be explained as follows. Let us assume that an aqueous solution containing ions is injected into a chromatographic system equilibrated with a weak-acid-based eluent. As the sample reaches the head of the column, the solute anions become adsorbed to the stationary phase by displacing a certain amount of mobile phase anions. The latter as well as counter-ions and some undissociated molecules of the weak acid start moving along the column at the flow rate of the eluent. As the band has a composition different from that of the bulk eluent, it causes a change of the detector signal resulting in an extraneous peak on the chromatogram [2, 4]. In the present paper the peak is referred to as the system peak as it reflects the disturbance of the equilibrium of the chromatographic system. In literature it is often called injection peak [2, 4] in order to distinguish it from another peak characterizing the system (eluent/sample) and appearing on the chromatogram under certain conditions.

If samples of low ion concentration are analysed, the detection limit can often become the main problem. For example, in case of most advanced semiconductor factories or nuclear power plants, highly purified water is needed, in which only ppt level anions or cations are allowed as contaminants [8]. Pre-concentration to the levels enabling reliable detection is time-consuming and may distort the sample.

If the analytes are dissolved in the eluent, the system peak will always be the largest on the chromatogram. If one could show that a regular dependence exists between the area of the system peak and the anion concentration of the sample, it would be possible to lower the detection limit of the total concentration of anions through the system peak.

In a number of papers the system peak has been associated with the cation difference between the eluent and sample solutions, but the dependence between the anion concentration and the system peak area is still obscure. There is at least one reference in literature on using the system peak for the determination of the total ion content of the sample [9], but no measurements near the detection limit have been presented before the present paper. Thus, the relationship between the system peak and the system is indeterminate, and consequently little attention has been paid to the information inherent in the system peak.

First, the dependence between the system peak area and the analysed anions was examined. Proceeding from the results of that investigation and the above-mentioned fact of the system peak being largest in certain conditions, attempts were made to confirm the hypothesis that the system peak can be used for the determination of the total anion amount of the analysed sample. This would prove useful if the areas of the peaks directly related to the injected solutes were not reproducible or were buried in the detector noise.

EXPERIMENTAL SECTION

Instruments. The chromatographic systems included the following components: Perkin–Elmer-series 3B liquid chromatograph, Knauer conductivity detector, home-made anion-exchange column.

Materials. The eluent consists of 1.3 mM phtalic acid plus 0.9 mM Na_2CO_3 in bidistilled water. The flow rate of the eluent was maintained at 1.0 ml/min. All the solutions were prepared in the eluent. All salts used were of analytical grade.

All the chromatograms were registered by computers. The data analyses were performed using commercial and home-made programs.

For the examination of the behaviour of the system peak the following solutions were prepared: each solution contained Cl^-, NO_3^-, SO_4^{2-} ions in ratios 1:1:1.5. The solutions differed from mobile phase not only in their anion content but also in their concentration of the Na^+ ion. Solutions were prepared with the following anion concentrations: 0, 5, 10, 25, and 50 ppm.

To measure the detection limit, the salts analysed were dissolved in the eluent. The total anion concentration of the resulting solution was 20 ppm; it comprises Cl^-, NO_3^-, and SO_4^{2-} anions in a ratio 1:1:2. The original solution was gradually diluted. The anion concentrations of the resultant solutions were 2, 0.4, 0.04, and 0.004 ppm, respectively.

At each concentration at least three parallel measurements were made. All the experiments were registered and the data analysed in a computer. At each concentration the variation coefficient for each peak was calculated.

RESULTS AND DISCUSSION

The behaviour of the system peak on chromatograms was observed adding to the sample solution small amounts of sodium carbonate solution (in known volumes). On the first chromatogram, the direction of the system peak was negative. Increasing the concentration of the Na^+ ion, the area of the system peak was decreased until the direction of the peak changed to positive and the area of the peak started to grow.

Calculations showed the amount of Na_2CO_3 necessary to eliminate the system peak to be decreasing as the anion content of the sample solution rises. The increase in the concentration of the Na^+ ion (caused by raising the concentration of the sample) was taken into account.

Figure 1 shows that the cation concentration needed to compensate for the negative system peak area also depends on the anion concentration of the analysed sample, not only on the difference between the cation content of the eluent and the sample solution.

The analysis of the data derived from chromatograms of samples with different anion concentration revealed a linear relationship between the system peak area and the total anion concentration of the sample (Fig. 2).

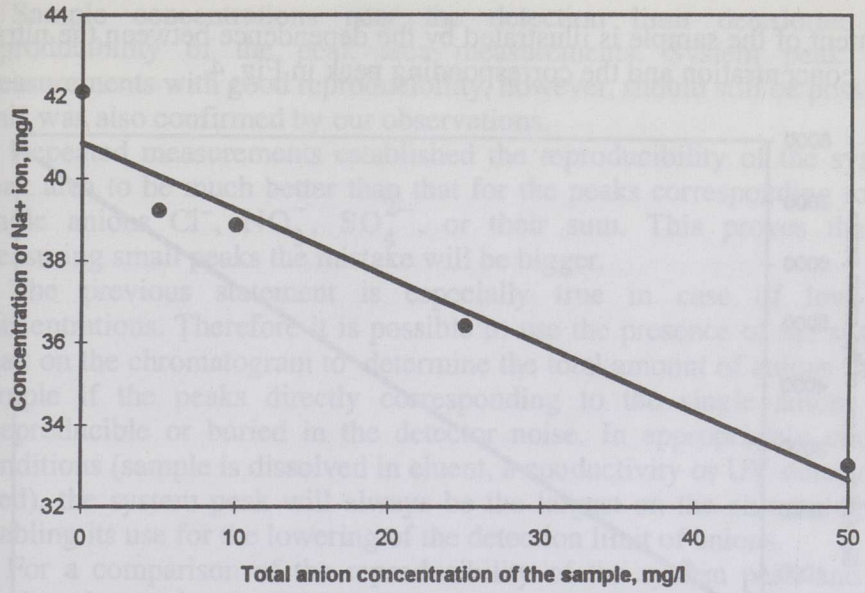

Fig. 1. The dependence between the anion concentration of the sample and the concentration of the Na^+ ion needed to eliminate the system peak.

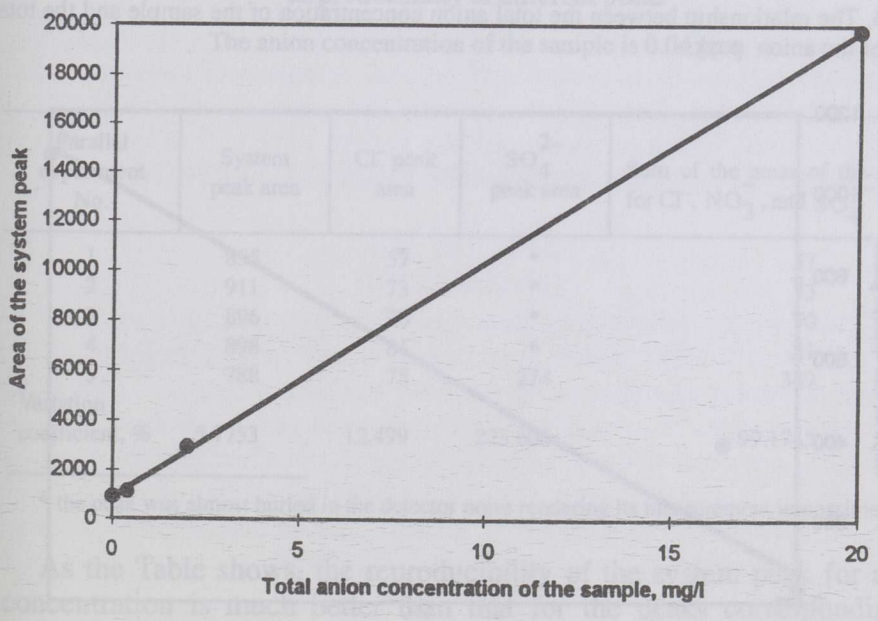

Fig. 2. The dependence of the area of the system peak on the total anion concentration of the sample.

Figure 3 shows the relationship between the total peak area directly corresponding to the single anions and the total anion content of the sample. The relationship between the single anion peak and the total anion

content of the sample is illustrated by the dependence between the nitrate-ion concentration and the corresponding peak in Fig. 4.

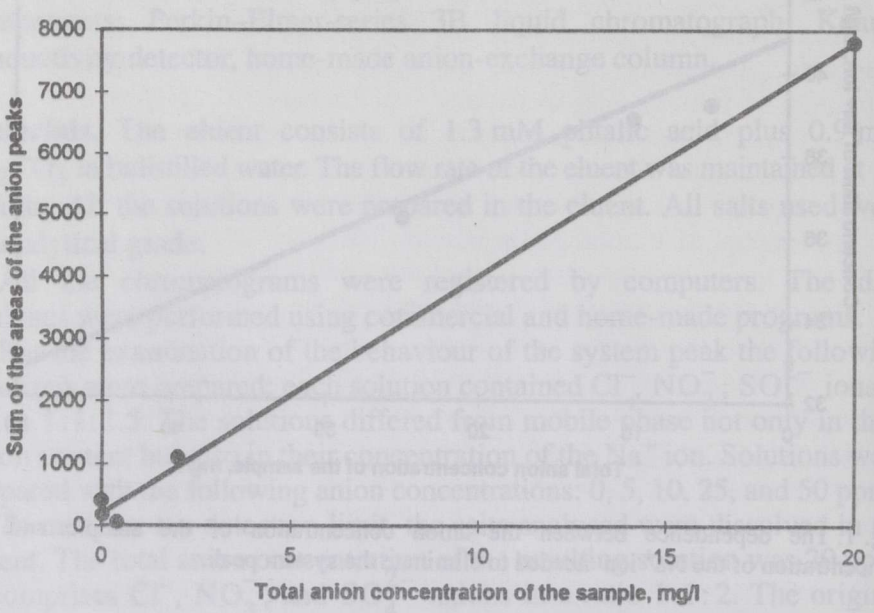

Fig. 3. The relationship between the total anion concentration of the sample and the total area of the anion peaks.

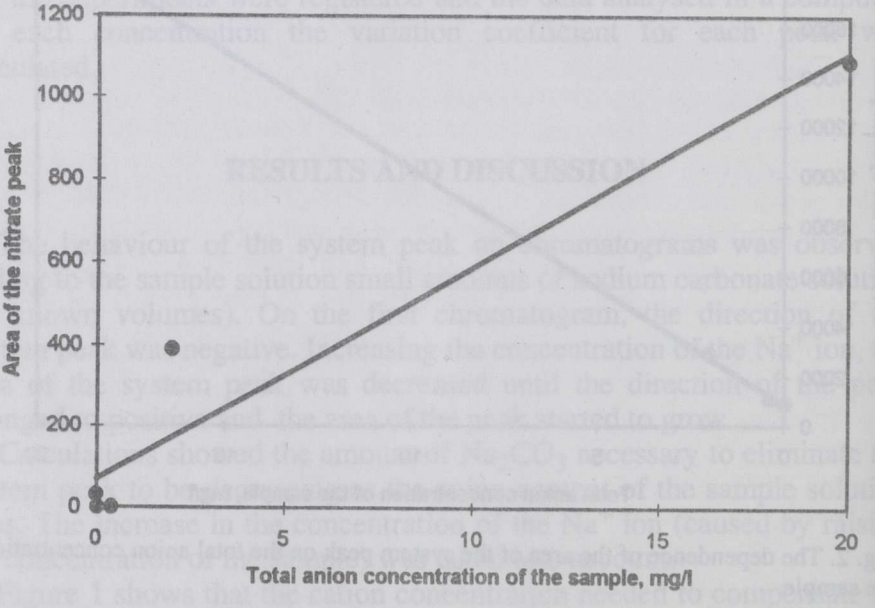

Fig. 4. Relationship between the nitrate ion and the corresponding peak.

As can be seen from Figs. 2–4, the correlation between the area of the system peak and the total anion concentration of the sample is remarkably better than the correlation between the system peak area and the single anion peak or the sum of the anion peaks.

Sample concentrations near the detection limit deteriorate the reproducibility of the peak area measurements. System peak area measurements with good reproducibility, however, should still be possible. This was also confirmed by our observations.

Repeated measurements established the reproducibility of the system peak area to be much better than that for the peaks corresponding to the single anions Cl^-, NO_3^-, SO_4^{2-}, or their sum. This proves that in measuring small peaks the mistake will be bigger.

The previous statement is especially true in case of low ion concentrations. Therefore it is possible to use the presence of the system peak on the chromatogram to determine the total amount of anions in the sample if the peaks directly corresponding to the single anions are irreproducible or buried in the detector noise. In appropriately chosen conditions (sample is dissolved in eluent, a conductivity or UV-detector is used), the system peak will always be the largest on the chromatogram enabling its use for the lowering of the detection limit of anions.

For a comparison of the reproducibility of the system peak and the single anion peaks, the Table presents a set of parallel experiments with a variation coefficient for every peak on the chromatogram.

Reproducibility of different peaks

The anion concentration of the sample is 0.04 ppm

Parallel experiment No.	System peak area	Cl^- peak area	SO_4^{2-} peak area	Sum of the areas of the peaks for Cl^-, NO_3^-, and SO_4^{2-} ions
1	855	57	*	57
2	911	73	*	73
3	896	70	*	70
4	898	81	*	81
5	788	75	274	349
Variation coefficient, %	5.7753	12.499	223.606	99.1745

* the peak was almost buried in the detector noise rendering its measurement impossible.

As the Table shows, the reproducibility of the system peak for a low concentration is much better than that for the peaks corresponding to single anions. The Table gives no data on the peak corresponding directly to the NO_3^- ion as its detection was not possible at that concentration.

The results presented in the paper also indicate that there are conditions in which the system peak area (which depends both on the total cation concentration of the sample and the eluent) can be significantly smaller than expected or disappears completely from the chromatogram (see Fig. 1). Our results indicate that, fortunately, this will not happen if the sample analysed is dissolved in the eluent. On the other hand, the

possibility of removing the system peak from the chromatogram by adding a predetermined amount of Na^+ ions to the sample solutions can also be utilized for performing certain measurements.

First, it can be used to improve the determination of the early-eluting ions frequently masked by system peaks of large amplitude. Secondly, it can be utilized in correlation ion chromatography [10], in a method for low concentration sample measurements where the sampling irreproducibility generates variations of the system peak area. The variations in turn generate disturbances of the base-line of the chromatogram, thus masking the small peaks. Reduction of the system peak is of paramount importance in correlation ion chromatography as it can greatly improve the results. Since ion chromatography is a separation method, the advocating of such a nonspecific parameter as the area of the system peak to characterize the water sample might seem irrelevant. Moreover, there are other methods available for the characterization of the water nonvolatile residue (NVR), where dissolved salts are a main component. Conventional NVR-monitoring tools include either evaporation-gravimetric determination (which is a slow and inaccurate technique) or the use of a sophisticated nucleus counter for counting the particles produced by the evaporation of the fine droplets of the sample in the atomizer [11]. System peak area measurement for NVR characterizations can be recommended for laboratories where ion chromatography is routinely implemented and where the concentration of the individual ions is no concern. If the concentration of the sample falls below the detection limit and the areas of the peaks corresponding to the individual ions cannot be measured, the system peak still offers a simple, rapid, and accurate characterization of the sample NVR.

CONCLUSION

The system peak or injection peak as it is often called in literature can be used for the determination of the total anion concentration in samples where the concentration of one or more solutes is under the detection limit. Moreover, as the reproducibility (characterized by the variation coefficient) is much higher for the system peak than for the peaks corresponding to the single anions, it is possible to improve the precision of the measurements for water parameters like NVR.

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SÜSTEEMIPIIK IOONIKROMATOGRAAFIAS

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Süsteemipiik, mida kirjanduses sageli nimetatakse ka sisestuspiigiks, sobib anioonide summaarse kontsentratsiooni määramiseks lahustes, milles ühe või enama aniooni kontsentratsioon on allpool aniooni detekteerimispiiri. Kuna süsteemipiigi reprodutseeritavus (seda iseloomustab variatsioonikoefitsient) on tunduvalt parem kui otseselt üksikutele anioonidele vastavate piikide oma, saab süsteemipiigi abil vähendada meetodi detekteerimispiiri ja tõsta mõningate vee parameetrite (näit. mittelenduv jääk) määramise täpsust.

ПИК СИСТЕМЫ В ИОННОЙ ХРОМАТОГРАФИИ

Рут КУЛДВЕЭ

В ионной хроматографии после ввода пробы нарушается равновесие, и переход системы в новое равновесие сопровождается появлением пиков – артефактов на хроматограмме, известных под

названием "пик системы". В работе изучены причины появления пика системы и соотношение между его площадью и концентрацией анионов в пробе. Показано, что площадь пика системы линейно связана с концентрацией анионов в пробе, и это обстоятельство можно использовать для оценки суммарной концентрации анионов, когда определение площадей индивидуальных пиков затруднено из-за шумов детектора.