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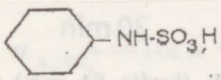
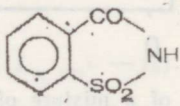
DETERMINATION OF SODIUM CYCLAMATE AND SACCHARIN BY ION CHROMATOGRAPHY

Introduction

Organic compounds, other than carbohydrates, that taste sweet have been known for a century. The list of these substances — sweeteners — now includes dozens of synthetic organic compounds [1]. A number of them are salts of organic acids which are easily soluble in water. The salts of (I) and (II) are especially widely used in Europe.



(I)
Cyclamic acid



(II)
Saccharin

This is probably due to the rather simple synthetic methods available for their industrial production.

In order to control the concentration of (I) and (II) in soft drinks and food, one needs a selective, inexpensive, and sufficiently sensitive analytical method for their determination. It has already been demonstrated [2] that such analyses may be performed by applying modern ion chromatography carried out with top level equipment manufactured by Dionex Corporation. However, the equipment used in [2] is not available to numerous chemists for economic reasons. We have developed an ion chromatographic method for the determination of (I) and (II) applying considerably cheaper equipment (see the Experimental section). The commercially available pieces of (I) and (II) are in fact mixtures of three or four components: (I) and/or (II); sodium bicarbonate, and tartaric acid. The last components are added to (I) and (II) in order to ensure a rapid dissolution of tablets in water.

Experimental

Materials. The sweeteners analysed were the sweetening tablets Süssli (Krüger & Co, Gladbach, Germany) and Huxolin (Huxol Kommanditgesellschaft, Seevetal, Germany). The saccharin used was a sodium salt of (I), from Minkhimprom, Moscow. The tartaric acid was analytically pure grade from Sojuzkhimreactiv, Moscow. The carbonate eluent was made from Na_2CO_3 and $NaHCO_3$, both analytically pure grade from Sojuzkhimreactiv, Moscow.

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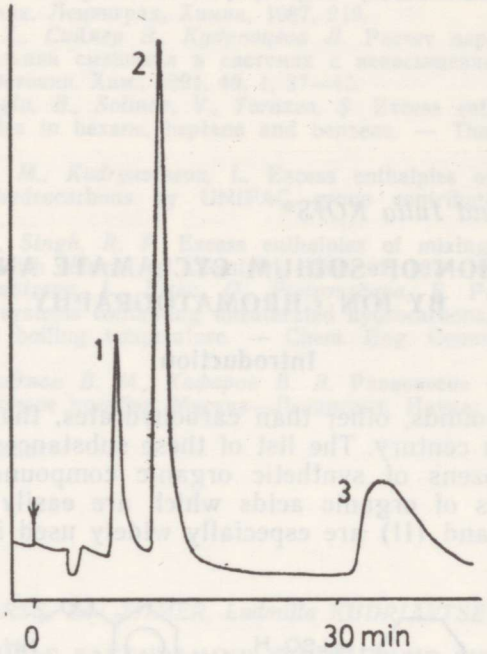

Fig. 1. Chromatogram of a mixture of Süssli (brutto 64 ppm), saccharin (273 ppm), and tartaric acid (76 ppm): *1* — cyclamic acid, *2* — tartaric acid, and *3* — saccharin. Eluent: 2.4 mM Na_2CO_3/3.0 mM $NaHCO_3$, flow rate 1.2 ml/min. Detector: 0.1 mS×100.

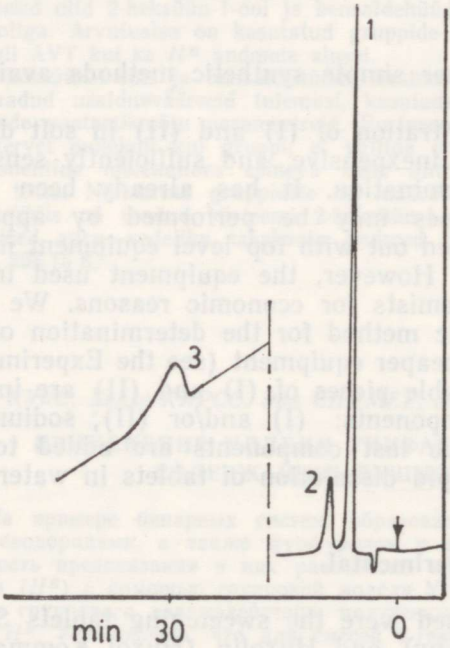

Fig. 2. Chromatogram of Süssli (brutto 248 ppm, i. e. 1 tablet in 250 ml water): *1* — cyclamic acid (160 ppm), *2* — tartaric acid, and *3* — saccharin (16 ppm). Eluent: 2.4 mM Na_2CO_3/3.0 mM $NaHCO_3$, flow rate 1.5 ml/min. Detector: 1 mS×100. At the dashed line the detector's sensitivity was increased 10 times.

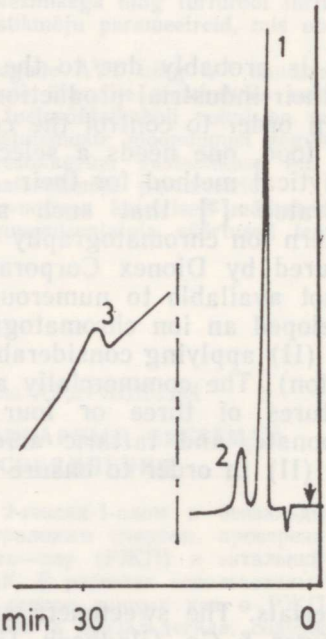

Fig. 3. Chromatogram of Huxolin (brutto 243 ppm, i. e. 1 tablet in 250 ml water): *1* — cyclamic acid (160 ppm), *2* — tartaric acid, and *3* — saccharin (16 ppm). Eluent: 2.4 mM Na_2CO_3/3.0 mM $NaHCO_3$, flow rate 1.5 ml/min. Detector: 1 mS×100. At the dashed line the detector's sensitivity was increased 10 times.

Equipment. An inexpensive ion chromatograph IVK-1 (Design Office of the Estonian Academy of Sciences, Tallinn) with the conductometric detector JD-1 was used. The separator column (4×250 mm) was packed with the resin HIKS-1 (*Hiiu Kalur*, Tallinn). This resin has low capacity: 0.0023 mmole/cm³. The suppressor column (4×250 mm) was packed with cationite Dowex WX16. The sample volume was 0.10 ml (Fig. 1) or 0.40 ml (Figs. 2 and 3). The recorder was a model RE 541 (BBC, Goerz) used at 2 mV/20 cm (full scale). The chromatograms were run with detector sensitivity 1 mS×100 and with the cell constant 7 cm^{-1}. The experimental conditions listed in the captions for Figs. 2 and 3 yielded the peak height for nitrate ions 3.3 mm/ppm NO_3.

Results and Discussion

The peaks on the chromatograms run were assigned using samples of various concentrations of (I), (II), and tartaric acid (see Fig. 1). The chromatograms of Süssli and Huxolin tablets are shown in Figs. 2 and 3. Applying the normal carbonate eluent (2.4 mM Na_2CO_3/3.0 mM $NaHCO_3$) and taking the SO_4^{2-} ions as reference we calculated the relative retention times:

$$\alpha_{A,\,SO_4^{2-}} = (t_{R,\,A} - t_0)/(t_{R,\,SO_4^{2-}} - t_0).$$

It should be noted that in the equation the void time, t_0, is that for the separator column (not including the void time for the suppressor column [3]). The following values of $\alpha_{A,\,SO_4^{2-}}$ were obtained: for (I) 0.43, for (II) 2.30, and for tartaric acid 0.84. Comparing these results with those from [2] we can state that (i) the column with HIKS-1 resin eliminates the need to use different chromatographic conditions for the determination of cyclamate and saccharin, and (ii) the determination of cyclamate is not disturbed by the presence of Cl^- ions, but by the presence of NO_3^- ions (on the HIKS-1 resin the retention times for (I) and NO_3^- ions are practically equal).

The sensitivity of the conductometric detection system (detector + recorder) at the standard settings (see the Experimental section and the captions for Figs. 2 and 3) was rather low: for (I) 0.91 mm/ppm (I) and for (II) 0.069 mm/ppm (II). In the case when the sensitivity was increased 10 times, the baseline drift became rather big (see Figs. 2 and 3).

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NAATRIUMTSÜKLAMAADI JA SAHHARIINI IOONKROMATOGRAAFILINE MÄÄRAMINE

On esitatud ioonkromatograafiline metoodika kahe magusa aine — naatriumtsüklamaadi ja sahhariini — määramiseks nende vesilahustes.

Юло ХАЛДНА, Юлия КОЙС

ИОНОХРОМАТОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦИКЛАМАТА НАТРИЯ И САХАРИНА

Предложена методика ионохроматографического определения двух сладких соединений — цикламата натрия и сахарина — в их водных растворах.