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Ion-exchange separation of inorganic anions on a HEMA 1000 Q-L column

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ABSTRACT

The polymeric anion-exchange material HEMA 1000 Q-L was used to separate common inorganic anions. The effect of the experimental conditions on the separation was studied in detail and compared with the model of dynamic ion exchange in ion-pair reversed-phase chromatography. The separation on HEMA Q-L is governed by a combination of anion exchange at fixed sites and solvophobic interactions. The optimum conditions involve the use of an aqueous sulphosalicylate mobile phase of pH × xe 4.5 and indirect UV photometric detection at 285 nm. The optimized method was applied to the determination of chloride, sulphate and nitrate in various natural and waste waters and the results were compared with independent values obtained by commercial ion chromatography and by potentiometry with a nitrate-selective electrode.

INTRODUCTION

Ion-exchange chromatography (IEC) is a commonly used method for the determination of inorganic cations and especially anions. Small *et al.* [1] substantially stimulated the development of IEC by introducing ion exchangers with a low ion-exchange capacity combined with effective suppression of the mobile phase electrical conductivity in a column packed with a strong ion exchanger of the opposite type, thus permitting the use of conductivity detection. Commercial equipment for this method, under the name ion chromatography, has become widely available, primarily from Dionex (*e.g.*, [2–5]).

Low ion-exchange capacities permit rapid mass transfer in the separation system and thus improve the separation efficiency. Depending on the matrix sorbent, low-capacity ion-exchange columns can be divided into two groups, silica-based and resin-based, the latter having an advantage of applicability over a wider pH range.

This paper describes the separation of a number of common anions on a newly developed anion exchanger HEMA Q-L [6,7], which is based on a matrix of a hydroxyethyl methacrylate copolymer modified with epoxy groups and containing triethylamino groups as the ion-exchange sites. The material exhibits a low specific exchange capacity of 0.6–0.9 mmol/g, excellent chemical stability and good mechanical strength. We have studied the effects of the aqueous mobile phase composition, its

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ionic strength and pH and the effects of the presence of organic modifiers and ion-pairing agent (cetyltrimethylammonium bromide, cetrimide) in the mobile phase on the retention of common inorganic anions on this stationary phase. The results have been compared with those obtained [8] in the separation of these anions in a reversed-phase system of a C_{18} stationary phase and a mobile phase containing cetrimide as the ion-pairing agent, citrate as the counter ion and methanol as the organic modifier. The optimized separation using HEMA Q-L was applied to determination of chloride, sulphate and nitrate in various natural and waste waters.

EXPERIMENTAL

Chemicals

All the chemicals employed were of analytical-reagent grade from Lachema (Brno, Czechoslovakia) and were used as received. Doubly distilled water was used throughout.

Stock solutions of the test anions were prepared by dissolving the substances (sodium or potassium salts) either in water or in a particular mobile phase. Their concentrations corresponded to 1–2 mg per 10 ml and the solutions were appropriately diluted immediately before use.

The mobile phases were degassed in an ultrasonic bath and by passage of helium.

Apparatus

The liquid chromatographic system involved a Model 2150 pump and a Model 2151 variable-wavelength UV–VIS detector (LKB, Bromma, Sweden), a Rheodyne (Cotati, CA, U.S.A.) Model 7125 injector with 10- and 20-μl loops, a CDCL 1 conductimetric detector, an ADLC 1 amperometric detector with a carbon-fibre array working electrode [9], a stainless-steel counter electrode and an Ag/AgCl (saturated) reference electrode and a TZ 4200 dual-line chart recorder (all from Laboratorní Přístroje, Prague, Czechoslovakia). The conductimetric detector was operated using an a.c. voltage at a frequency of 80 Hz. The amperometric measurements were carried out in the oxidation mode at + 1.1 V [*vs.* Ag/AgCl (sat.)].

Glass columns (150 × 4 mm I.D.) were packed with Separon HEMA 1000 Q-L strongly basic, low-capacity, anion exchanger (10 μm) (Tessek, Prague, Czechoslovakia). The mobile phase flow-rate was maintained at an optimal value of 0.5 ml/min. Prior to use, the columns were equilibrated with a particular mobile phase overnight.

All the measurements were carried out at laboratory temperature, at least in triplicate.

RESULTS AND DISCUSSION

Separation

Mobile phase composition. Three aqueous mobile phases were used. Eluent anions of different character, namely, $4 \cdot 10^{-2}$ *M* acetate, $4 \cdot 10^{-3}$ *M* citrate and $5 \cdot 10^{-4}$ *M* sulphosalicylate, were tested at pH 7.6 (Fig. 1). It can be seen that the structure of the eluent anion has decisive effect on the eluting strength of the mobile phase. The HEMA stationary phase has both ion-exchange and hydrophobic prop-

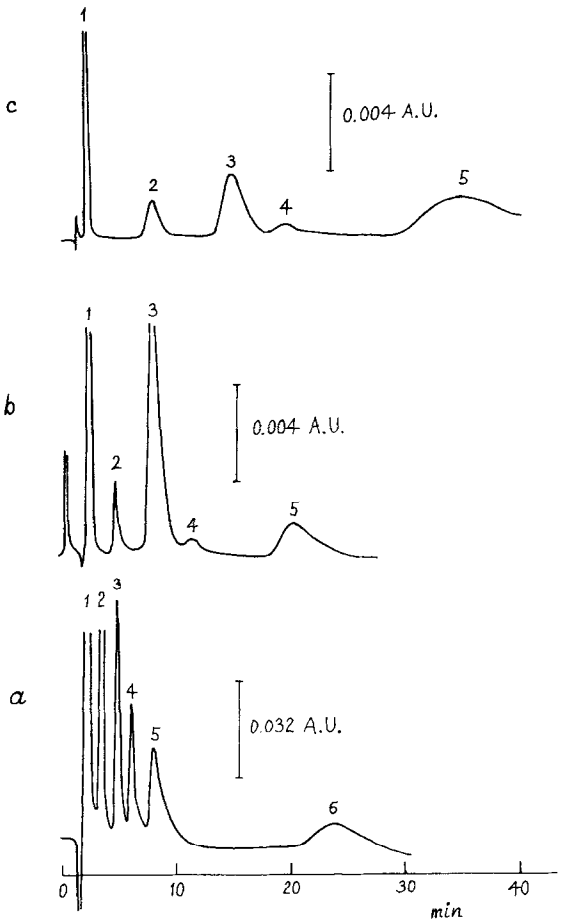

Fig. 1. Effect of the eluent structure on its eluting strength. Mobile phase: (a) 0.5 m*M* sulphosalicylate, pH 7.6; (b) 4 m*M* citrate, pH 7.5; (c) 40 m*M* acetate, pH 7.6. UV photometric detection at (a) 285, (b) 210 and (c) 220 nm. 1 = IO_3^-; 2 = BrO_3^-; 3 = NO_3^-; 4 = NO_2^-; 5 = Br^-; 6 = I^-.

erties; therefore, the greatest affinity toward HEMA is exhibited by sulphosalicylate, containing a benzene ring and being the least polar. Citrate and acetate then have progressively lower affinities toward HEMA. Consequently, the mobile phase containing sulphosalicylate has the highest eluting strength, even when the concentration of the eluent anion is eight and eighty times lower than those in the other mobile phases.

Mobile phase pH. The effect of the mobile phase pH was studied over the pH range 3.4–7.6 with acetate and sulphosalicylate mobile phases. At low pH, the non-ionized organic acids predominate in the mobile phases and cause a decrease in the eluting strength; the eluting strength gradually increases with increasing pH, as the concentration of the eluent free anions increases (Fig. 2). However, compared with the reversed-phase system (Fig. 2 in ref. 8), the effect of pH on the anion retention is less

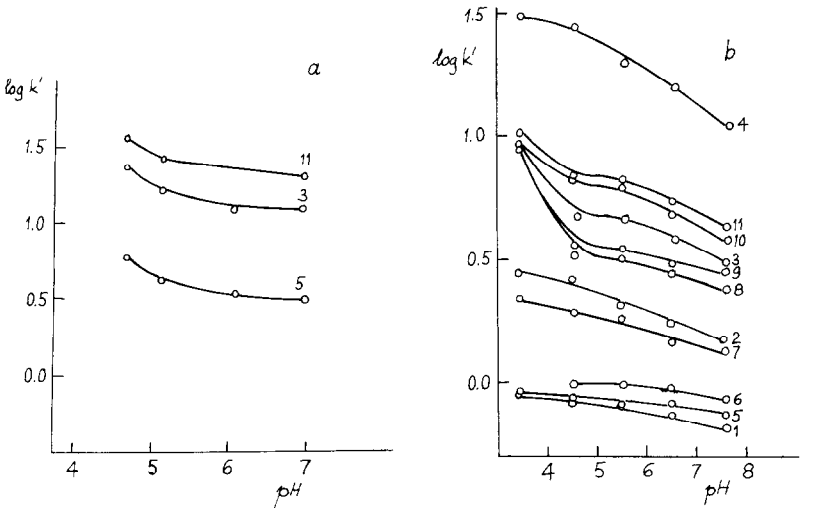

Fig. 2. Dependences of log k' on mobile phase pH. Mobile phase: (a) 10 mM acetate; (b) 0.5 mM sulphosalicylate. 1 = F^-; 2 = Cl^-; 3 = Br^-; 4 = I^-; 5 = IO_3^-; 6 = CN^-; 7 = BrO_3^-; 8 = NO_2^-; 9 = SO_4^{2-}; 10 = ClO_3^-; 11 = NO_3^-.

pronounced. The pH strongly affects the separation efficiency; a higher pH is generally preferable from this point of view, as illustrated in Fig. 3. The mobile phase pH also affects the sensitivity of photometric detection with the sulphosalicylate mobile phase, as shown below.

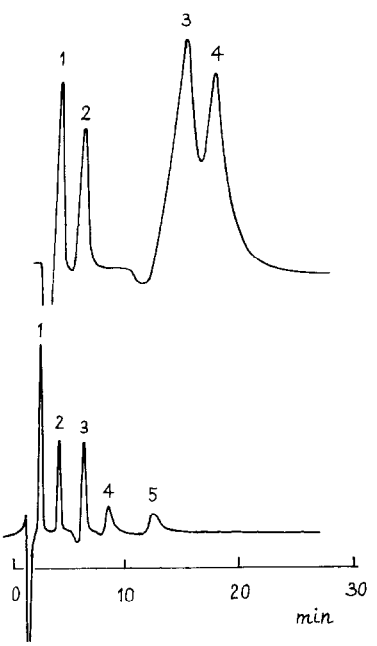

Fig. 3. Effect of the mobile phase pH on the separation efficiency. Mobile phase: 0.5 mM sulphosalicylate of (a) pH 3.4 and (b) pH 4.5. 1 = IO_3^-; 2 = BrO_3^-; 3 = NO_2^-; 4 = Br^-; 5 = NO_3^-.

Eluent concentration and mobile phase ionic strength. The dependences of the logarithms of the capacity factors, log k', on the logarithm of the eluent anion concentration, log c_E, are linear, as predicted by the equation

$$\log k' = p + q \log c_E$$

derived by Vláčil and co-workers [7,10] for HEMA. Fig. 4 depicts these dependences for the acetate mobile phase.

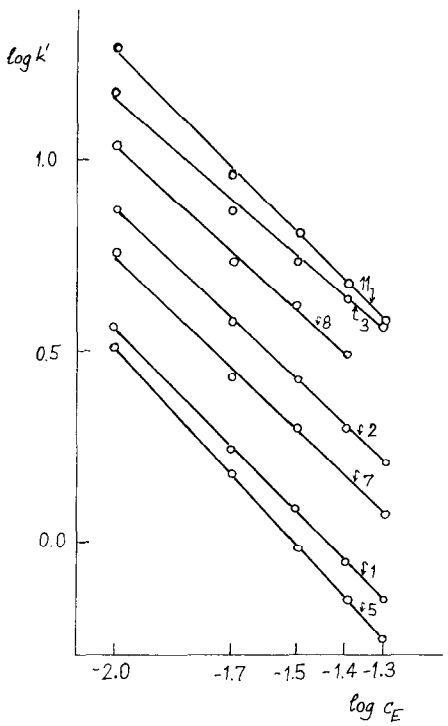

Fig. 4. Dependences of the log k' on log (eluent concentration). Mobile phase: acetate (pH 7.0). Ions as in Fig. 2.

The effect of the mobile phase ionic strength, μ, adjusted by additions of Na_2HPO_4, on the anion retention was plotted as $1/k'$ *vs.* $1/\mu^{1/2}$ (Fig. 5) in order to permit direct comparison with Fig. 5 in ref. 8 for a reversed-phase system. While the dependence in ref. 8 reflects a combination of the effects of an electrical double layer formed [11] and competitive ion exchange within this double layer, the plot in Fig. 5 in this paper corresponds to simple ion exchange at the fixed sites of the stationary phase (however, at higher ionic strengths the HPO_4^{2-} anion begins to compete with the eluent anion).

Effects of organic modifiers and of an ion-pairing agent. It has been found that organic solvents do not significantly affect the retention behaviour of the studied

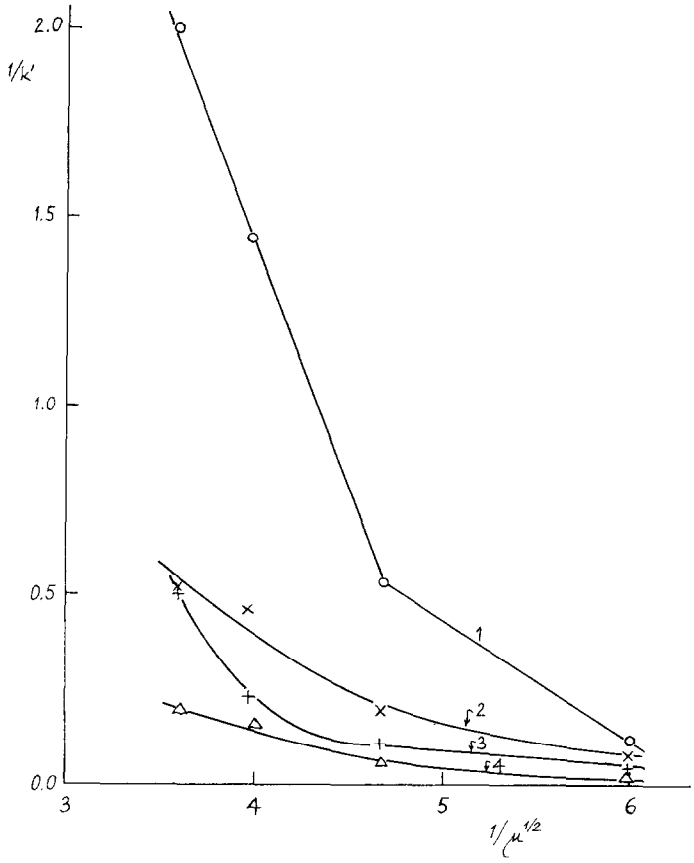

Fig. 5. Dependences of the reciprocal of the capacity factor on the reciprocal of the square root of the ionic strength. Mobile phase: 0.01 *M* acetate (pH 7.0) with various concentrations of Na_2HPO_4. 1 = NO_3^-; 2 = NO_2^-; 3 = BrO_3^-; 4 = IO_3^-.

anions when present at moderate concentrations in the mobile phase [methanol, acetonitrile, acetone and isopropanol were tested in the range 0–20% (v/v)]. This contrasts sharply with the situation in the ion-pair reversed-phase system [8], where the dependence of the capacity factors on the organic modifier content is complex (Fig. 4 in ref. 8).

However, the presence of an organic modifier, *e.g.*, methanol, has a greater effect when an ion-pairing agent, here cetrimide, is present. It can be seen from Table I that the presence of cetrimide in the aqueous mobile phase leads to a slight increase in the capacity factors of the solutes and that this increase is enhanced by addition of methanol to the mobile phase.

The hydrophobic properties of the HEMA material are again responsible for these effects: cetrimide is adsorbed on the HEMA surface, creating additional ion-exchange sites due to the formation of an electrical double layer similar to that in the ion-pair reversed-phase (IP-RP) system [8]. The presence of methanol supports the

TABLE I

CAPACITY FACTORS OF ANIONS IN VARIOUS MOBILE PHASES

Anion	Mobile phase[a]		
	I	II	III
IO_3^-	0.69	0.72	1.01
BrO_3^-	1.48	1.86	2.50
ClO_3^-	4.32	5.45	7.27
F^-	0.75	0.78	0.94
Cl^-	1.70	1.84	2.63
Br^-	3.65	4.29	5.26
I^-	10.81	12.50	15.20
NO_2^-	2.47	3.34	4.10
NO_3^-	4.62	5.61	7.55
SO_4^{2-}	3.77	3.87	5.62
$H_2PO_4^-$	1.13	1.43	1.89
Formate	1.03	1.27	1.55
Propionate	1.09	1.29	1.48
Butyrate	1.48	1.72	1.98
Pentanesulphonate	3.72	3.99	4.60

[a] Mobile phases: I = 0.04 *M* acetate; II = 0.04 *M* acetate–0.1 m*M* cetrimide; III = 0.04 *M* acetate–0.1 m*M* cetrimide–10% (v/v) methanol.

adsorption of cetrimide on the HEMA material and simultaneously suppresses the affinity of the ionic solutes toward the mobile phase, which becomes less polar. Hence, in the presence of ion-pairing agents and organic solvents, the properties of the HEMA ion-exchange system become more similar to IP-RP systems, one of which was studied previously [8].

It can be concluded that the comparison of the previous results [8] and the present results supports the model of dynamic ion exchange in the IP-RP system (for a detailed discussion see ref. 8) and shows that, on the other hand, the separation on the HEMA 1000 Q-L anion exchanger is also affected by solvophobic interactions similar to those operating in the IP-RP system. The selectivities and separation efficiencies in the two systems are similar and the HEMA 1000 Q-L stationary phase seems to be better suited to practical work, as the separation system is simpler, better defined and does not require prolonged equilibration prior to use, which is essential for the formation of a steady-state double layer on the reversed phase.

Detection

Three detection methods, conductimetry, amperometry in the oxidation mode and UV photometry, were compared in our previous study (see Table I and Fig. 6 and their discussion in ref. 8). No method was found to be generally superior to the others. In practice, the detection techniques must be selected and sometimes combined depending on the particular analytical requirements. Conductimetry is universal and simple; on the other hand, the measuring sensitivity is sometimes insufficient. Amperometric detection is highly sensitive, but also very selective. UV photometry is more sensitive than conductimetry and exhibits a certain selectivity; moreover, it is

TABLE II

PRECISION OF DETECTION[a]

Anion	Conductometric (μA)			Amperometric (μA)			UV photometric (absorbance)		
	$\bar{s}$	R.S.D. (%)	n	$\bar{s}$	R.S.D. (%)	n	$\bar{s}$	R.S.D. (%)	n
Cl^-	18.2	3	8	–	–	–	–	–	–
BrO_3^-	61.0	4	8	–	–	–	0.22	9	7
NO_3^-	22.2	4	8	–	–	–	0.72	1	6
SO_4^{2-}	17.9	6	8	–	–	–	–	–	–
ClO_3^-	17.0	6	8	–	–	–	–	–	–
NO_2^-	–	–	–	294	6	11	0.51	4	7
I^-	–	–	–	264	4	6	0.60	3	6
SO_3^{2-}	–	–	–	10.6	7	5	0.32	5	8
SCN^-	–	–	–	82.1	3	6	0.48	2	6
S^{2-}	–	–	–	313	5	5	–	–	–
IO_3^-	–	–	–	–	–	–	0.44	4	4
$S_2O_3^{2-}$	–	–	–	–	–	–	0.48	4	6
CN^-	–	–	–	–	–	–	0.21	1	6

[a] $\bar{s}$ = Mean signal value; R.S.D. = relative standard deviation; n = number of measurements. Mobile phase, 0.1 m*M* cetrimide–4 m*M* citric acid–30% (v/v) methanol (pH 5.5).

possible to employ either direct photometry (*i.e.*, measurement of the solute absorbance on a low mobile phase background) or indirect measurement (*i.e.*, a negative peak is obtained for a less absorbing solute on a high background absorbance).

As can be seen in Table II, the precisions of the three detection methods are

TABLE III

DETECTION LIMITS (ng) OF INORGANIC ANIONS IN DIFFERENT MOBILE PHASES

Detection limits defined as the absolute amount of analyte in the sample volume injected (20 μl) producing a signal equal to twice the peak-to-peak noise.

Anion	Mobile phase[a]		
	I	II	III
F^-	–	28	2
Cl^-	–	140	1.3
CN^-	–	–	1.7
SO_4^{2-}	–	520	3.4
IO_3^-	26[b]	42[b]	9.3
BrO_3^-	587[b]	270[b]	8.3
NO_2^-	99[b]	19[b]	4.7
Br^-	2100[b]	1000[b]	7.5
ClO_3^-	–	1100[b]	14
NO_3^-	380[b]	2500[b]	14
I^-	–	–	75

[a] Mobile phase: I = 0.04 *M* acetate (pH 7.6) at 220 nm; II = 4 m*M* citrate (pH 7.6) at 210 nm; III = 0.5 m*M* sulphosalicylate (pH 7.6) at 285 nm.

[b] Positive response.

similar. For detection with the present system containing the HEMA 1000 Q-L ion exchanger, UV photometry is clearly the most suitable in common separations. Table III gives the limits of UV photometric detection, defined as the absolute amounts of analyte in the sample volume injected (20 μl) producing a signal equal to twice the peak-to-peak noise, for the three mobile phases studied. Table III demonstrates that the sulphosalicylate mobile phase, in addition to permitting the best anion separation (see above), also gives the highest sensitivity of measurement. With all the anions studied, the response is negative at 285 nm, where sulphosalicylate absorbs radiation very strongly. The detection sensitivity at 285 nm increases slightly with increasing pH of the mobile phase (Table IV), owing to enhanced ionization of sulphosalicylic acid and thus an increase in the concentration of the absorbing anion.

TABLE IV

DEPENDENCE OF UV DETECTOR SIGNAL ON pH

Mobile phase, 0.5 m*M* sulphosalicylate; measurement at 285 nm.

Anion	Signal (absorbance)				
	pH 3.45	pH 4.5	pH 5.5	pH 6.5	pH 7.6
IO_3^-	0.064	0.065	0.087	0.091	0.154
BrO_3^-	0.049	0.032	0.051	0.054	0.105
NO_2^-	–	0.031	0.035	0.038	0.085
Br^-	–	0.009	0.015	0.015	0.049
NO_3^-	–	0.0064	0.010	0.010	0.036
I^-	–	0.0025	0.003	0.005	0.006

Separation systems employing indirect detection are complicated by the system (vacancy) peaks (for a discussion see, *e.g.*, [12]). In our system, we usually observed two system peaks (see Figs. 1, 3 and 6). The first is independent of the mobile phase pH, is always positive and emerges at the column void volume; the other depends on the pH and can be either positive or negative. We assume that the former peak corresponds to the local high concentration of the sulphosalicylate anion, displaced from the stationary phase by the solutes injected, whereas the latter corresponds to non-ionized sulphosalicylic acid; with an increase in pH, the fraction of non-ionized sulphosalicylic acid in the mobile phase decreases and the corresponding system peak becomes smaller and finally disappears.

Application

The above results led to the optimum experimental conditions of the use of an aqueous mobile phase with pH $\geqslant$ 4.5 and indirect photometric detection at 285 nm. Under these conditions we analysed samples of various natural and waste waters for the ecologically important anions chloride, sulphate and nitrate. The samples involved spring waters from variously polluted locations (I, III, IV), a stream water (II), precipitation waters, collected either in an open area (VI) or in woods where the deposits were washed from the trees (V), Prague tap water (VII) and waste waters from

TABLE V

ANALYSIS OF WATER SAMPLES

A, this work; B, ion chromatography; C, potentiometry with a nitrate ion-selective electrode [values in parentheses, results after precipitation of chloride with silver sulphate (0.5 ml of 0.1 *M* Ag_2SO_4 per 10 ml of sample)].

Sample No.	Nitrate (mg/l)			Chloride (mg/l)		Sulphate (mg/l)	
	A	B	C	A	B	A	B
I	1.10	1.34	1.56 (1.08)	1.10	1.54	10.1	11.97
II	6.35	7.18	6.96 (5.53)	1.15	1.85	20.0	21.81
III	90.5	–	90.5 –	16.3	–	52.8	–
IV	51.2	–	51.0 –	23.2	–	55.7	–
V	5.89	7.17	5.53 (4.19)	1.00	1.00	13.5	14.58
VI	2.80	2.37	2.05 (1.56)	0.40	0.30	4.90	4.56
VII	55.8	–	50.0 –	7.40	–	49.4	–
VIII	27 800		34 800 –	70.0	–	–	–
IX	25 900		22 000 –	200	–	–	–

an electrotechnical factory (Tesle, Prague; VIII and IX). The results are summarized in Table V and a typical chromatogram is given in Fig. 6.

The results for nitrate were compared with those obtained by potentiometry with a nitrate-selective electrode; samples I, II, V and VI were further independently analysed on a commercial ion chromatograph in the laboratories of Geological Survey of Czechoslovakia in Prague. It can be seen from Table V that the agreement of all the results is satisfactory.

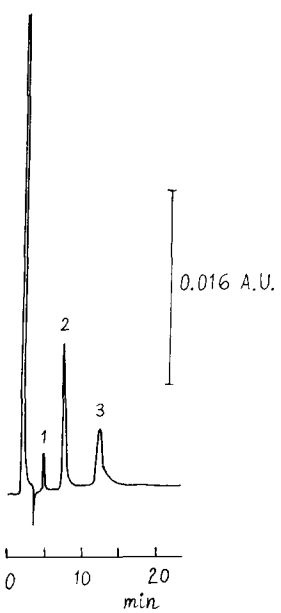

Fig. 6. Analysis of precipitation water (sample V). Mobile phase, 0.5 m*M* sulphosalicylate (pH 7.6); flow-rate, 0.5 ml/min. Detection, UV (285 nm); amount injected, 20 μl. 1 = Cl^-; 2 = SO_4^{2-}; 3 = NO_3^-.

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