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Note

Determination of inorganic main group anions by high-performance liquid chromatography

ROGER NEIL REEVE

Research and Development Department, Peabody Holmes Limited, Huddersfield, Yorkshire, HD1 6RB (Great Britain)

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High-performance liquid chromatography (HPLC) has not been widely used for the routine analysis of inorganic ions and there is no parallel to the rapid expansion of the use of the technique for organic and biochemical analyses. This can be traced to the poor detectability of most inorganic ions with the commonly used 254-nm ultraviolet (UV) detector. Ion-exchange techniques which have been used with inorganic systems[1–4] are inconvenient compared with reversed-phase ion-pair techniques now commonly used for organic systems[5,6]. Gel permeation, also occasionally used for inorganic ions[7–9], can give poor separation efficiency, whilst adsorption has had only specialised usage[10,11].

Reversed-phase techniques have only been used for inorganic species after reaction to form organic derivatives[11]. Direct analysis by ion-pair formation has not been attempted previously. Although many alternative forms of detection have been investigated for the determination of main group anions (including refractive index[7], chemical reaction with fluorimetric or UV[3,11] detection, conductivity with or without ion suppression[2,8], flame emission[4] and atomic absorption of derived complexes[9]), UV detection at 210–220 nm does not appear to have been investigated. Many inorganic ions exhibit strong absorption at these wavelengths[12]. The aim of the present note is to demonstrate the convenience of reversed-phase ion-pair techniques with low wavelength UV detection for the direct analysis of main group inorganic anions, a technique giving high detection sensitivity for a number of species together with good separation efficiency.

EXPERIMENTAL

Chemicals

Disodium hydrogen orthophosphate (AnalaR), potassium dihydrogen orthophosphate (AnalaR) and cetyl trimethyl ammonium bromide (cetrimide) were purchased from BDH (Poole, Great Britain). Methanol (reagent grade) was purchased from May & Baker (Dagenham, Great Britain), this being sufficiently pure for routine applications.

Salts for chromatographic examination (except sulphide and polythionates) were of the purest available commercial grade either as sodium or potassium salts.

Sodium tetrathionate dihydrate was purchased from Fluorochem (Glossop, Great Britain). Other polythionates were synthesised by standard procedures[13,14]. Sulphide solutions were freshly synthesised by passing hydrogen sulphide into aqueous sodium carbonate.

HPLC conditions

The chromatograph comprised of an Altex 110A pump (with Altex pulse damper), a variable wavelength Pye LC-UV detector and a Rheodyne 7010 loop injection valve (volume 10 μl); a detection wavelength of 215 nm was used. The 25 cm × 4.6 mm I.D. column was pre-packed with a cyano-bonded silica, Sil 60-D 10-CN (Chrompack, Middelburg, The Netherlands). The eluents, used at a flow-rate of 1.5 or 2.0 ml/min, were methanol–water mixtures (see Results and discussion), the solutions being 0.1 *M* Na_2HPO_4, 0.1 *M* KH_2PO_4 and 0.1% (w/v) cetrimide with respect to the aqueous component. The eluents were left one day before use, then filtered through 0.7 μm paper (Whatman, Maidstone, Great Britain) to remove precipitated impurities. Equilibration of the eluent with the column was very slow, taking several times more than the literature value of 52 column volumes for the similar palmityl trimethyl ammonium counter ion[6].

Samples (except sodium sulphide) were injected directly as aqueous solutions. Sulphide solutions were diluted with eluent before use and filtered to remove any precipitated sulphur impurity.

RESULTS AND DISCUSSION

Results are given in Tables I and II and examples of separation shown in Figs. 1–4. The elution order is the same for the two elution conditions, the effect of stronger eluent being merely to lessen the elution time of any species. For the monovalent ions, a similar order is found for the extraction of the species into organic solvents[15] (under conditions where nitrate precedes bromide) using quaternary ammonium and phosphonium salts, this in turn being similar to the affinity series for ion-exchange resins[16]. In both cases the dominant control has been attributed to the

TABLE I

RETENTION TIMES USING METHANOL–WATER (40:60) BUFFER AS ELUENT

Species	*Retention time (min)*	*Sensitivity sodium salt (ng)*
IO_3^-	1.94	5*
BrO_3^-	2.94	15*
HS^-	2.99	**
NO_2^-	3.40	1.2
HSO_3^-	3.52	**
N_3^-	4.09	10
NO_3^-	4.71	2
Br^-	5.99	90*
$S_2O_3^{2-}$	7.96	3
I^-	11.23	3*

* K salt.

** See Results and discussion.

TABLE II

RETENTION TIMES USING METHANOL–WATER (55:45) BUFFER AS ELUENT

Species	*Retention time (min)*	*Sensitivity sodium salt (ng)*
$S_2O_3^{2-}$	2.10	**
I^-	2.48	3*
$S_3O_6^{2-}$	3.27	81
$S_4O_6^{2-}$	5.24	5
$S_5O_6^{2-}$	6.57	6*

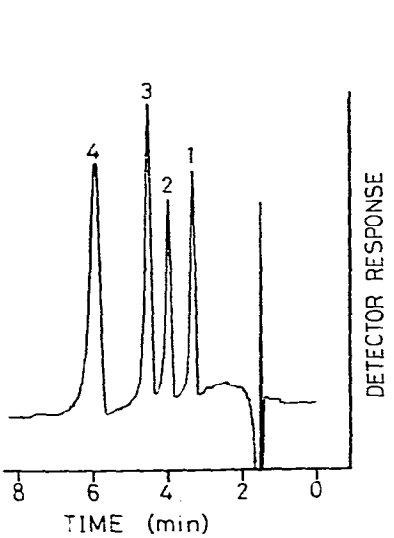
* K salt.

** The peak was too close to the solvent front to determine the ion at high sensitivity.

enthalpy of hydration of the ions[15]. Thiosulphate, however, could not be extracted into organic solvents whereas it is strongly retained under the conditions of Table I.

In order to produce the required separation the cetrimide was used in a much lower concentration than determined to be optimum for dyestuff separation[5]. A large buffer concentration was used to lower the required methanol content in order to allow injection of aqueous solutions with high salt concentrations. Initial experiments using tetrabutyl ammonium hydroxide as the ion-pair reagent were unsuccessful in separating weakly retained species in Table I from the solvent front.

Apart from the polythionates the inorganic ions could be separated with a single eluent (Table I) using the cyano-bonded column. Column efficiencies of 1300–5000 theoretical plates were achieved. Hydrosulphide and hydrosulphite gave broader peaks (Fig. 3) presumably due to reaction with traces of oxygen in the eluent. The reaction also precluded the determination of their sensitivity limits. Investigations using a more conventional ODS column (Spherisorb S10 ODS) with cetrimide were



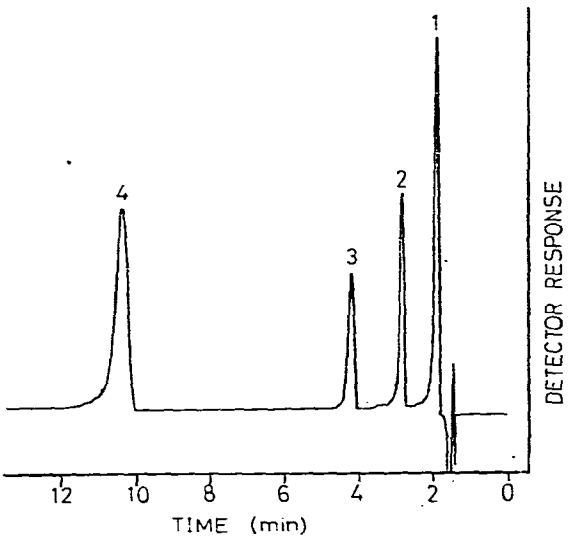


Fig. 1. Chromatogram of nitrogen anions and thiosulphate. 1 = Nitrite; 2 = azide; 3 = nitrate; 4 = thiosulphate. Conditions as in Table 1; flow-rate 2 ml/min.

Fig. 2. Chromatogram of halogen anions. 1 = Iodate; 2 = bromate; 3 = bromide; 4 = iodide. Conditions as in Table I; flow-rate 2 ml/min.

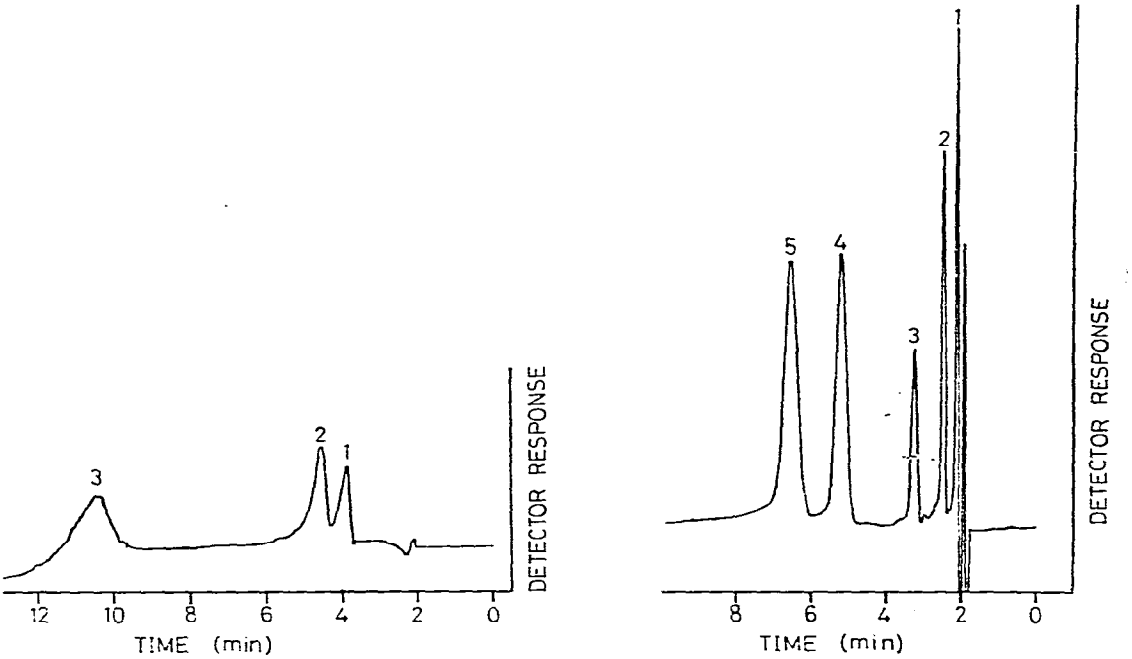


Fig. 3. Chromatogram of sulphur anions. 1 = Hydrosulphide; 2 = hydrosulphite; 3 = thiosulphate. Conditions as in Table I; flow-rate 1.5 ml/min.

Fig. 4. Chromatogram of iodide and polythionates. 1 = Thiosulphate; 2 = iodide; 3 = trithionate; 4 = tetrathionate; 5 = pentathionate. Conditions as in Table II; flow-rate 2 ml/min.

less successful. The ions could not be eluted under a single set of conditions. Peak shapes were also poor, giving at most a few hundred theoretical plates.

For many ions low wavelength UV gives a sensitive method of detection to nanogram level. Species found to be transparent, however, include sulphate and chloride. The small elution range (under conditions where few organic compounds would interfere) opens the technique for qualitative identification as well as quantitative analysis of the ions. This provides an advantage over ion-exchange techniques, the conditions of which are in general too specific for use for qualitative purposes. The diversity of the species separated in this work suggests the technique is quite general and may be extended to other main group species, giving a wide potential future usage.

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