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Short communication

Use of mordenite columns in ion-exclusion chromatography

B.K. Glòd^a, G. Perez^{b,*}, A.A.G. Tomlinson^c

^aPolish Academy of Sciences, Medical Research Centre, Dworkowa 3, 00-784 Warsaw, Poland

^bIstituto di Cromatografia del CNR, c.p. 10, 00016 Monterotondo Stazione, Rome, Italy

^cIstituto di Chimica dei Materiali del CNR, c.p. 10, 00016 Monterotondo Stazione, Rome, Italy

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Abstract

The separation of nitrite from nitrate ion by ion-exclusion chromatography has been carried out on a laboratory-made mordenite column. The results show that this cheap solid acid can replace, at least in this analysis, the commercial polysulphonated resins and that the separation between these two anions of environmental concern can be carried out very rapidly on such a column.

Keywords: Mordenite; Zeolites; Water analysis; Nitrite; Nitrate; Inorganic cations

1. Introduction

Although synthetic zeolites are widely used as molecular sieves in gas chromatography, their application in other chromatographic techniques is as yet undeveloped. The same is true of other porous materials, which are strictly connected to gas chromatography [1,2] following the popularity of the commercial product bentone-34 in the field. The only exceptions to this rule appear to be X and Y zeolites, which have been employed for separating monosaccharide–water mixtures [3].

Mordenite [4] is one of the best known acid zeolites, with a well-developed pore chemistry. It possesses straight, 12-membered channels of dimensions 6.7×7.0 Å which are connected by non-intersecting 8-membered ring channels of dimension 2.9×5.7 Å. Mordenite acts as a catalyst in protonation reactions of alkanes, alkenes and arenes, which

require Brønsted acid sites. A typical example is the protonation of adsorbed terpenes, where electron paramagnetic resonance techniques have demonstrated that stable carbocations are formed [5].

Ion-exclusion chromatography (IEC) is the technique of choice for separating ionic compounds [6], and some 10% of all ion chromatography determinations are now performed by ion-exclusion chromatography. The supports are usually based on a macro-porous styrene–divinylbenzene copolymer, i.e., a typical ion-exclusion chromatographic column consists of a totally sulphonate resin with high cation-exchange capacity. The resin is prepared by the catalytic polymerisation of a mixture of styrene and emulsified divinylbenzene, and subsequently treated with sulphuric acid to give about 80% of aromatic ring sulphonation.

Owing to the acidity of mordenite, we have substituted the usually employed resins with this inorganic material. To assess its utility, we selected the nitrate/nitrite ion separation because of its

*Corresponding author.

importance to the quality of food. Mordenite not only permits efficient separation of $\text{NO}_3^-/\text{NO}_2^-$ (not readily accomplished on other supports) it also provides a simple analytical method for the simultaneous determination of these ions.

2. Experimental

2.1. Materials

Mordenite was an Engelhardt product. Analytical reagent-grade sulphuric acid (Carlo Erba, Italy) dissolved in triply distilled water at the selected concentration was used as mobile phase. Sodium nitrate and sodium nitrite were research grade products (Carlo Erba).

2.2. Apparatus

The chromatographic analyses were carried out on a Beckman equipment consisting of a 110B Solvent Delivery Module, a 340 Organizer and a 160 Absorbance Detector. The retention times of the eluted compounds, detected at 200 nm, were measured using a Hewlett-Packard HP 3394A Integrator.

2.3. Procedure

Triply distilled water was passed through a Millipore (Bedford, MA, USA) Milli-Q water purification system, filtered through a Millipore 0.45- μm membrane filter and degassed in an ultrasonic bath, before the addition of sulphuric acid. The column was equilibrated for 1 h before use. All the analyses were carried out at room temperature.

A glass column (70 \times 6.8 mm I.D.) was filled with mordenite (160–200 mesh) using the dry method.

A real, not-drinking water sample, collected in our campus, was concentrated under vacuum before analysis.

3. Results and discussion

Fig. 1 shows a typical separation of nitrite from nitrate ions on mordenite; the two ions are eluted with a good separation. Given the importance of

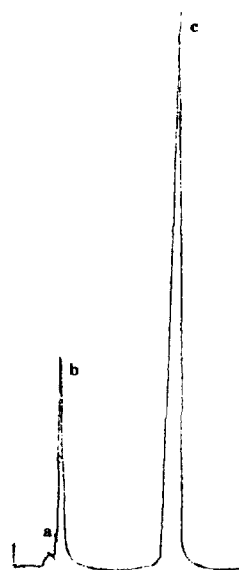


Fig. 1. Nitrite/nitrate separation on a 70 mm mordenite column. Mobile phase, 10 mM H_2SO_4 ; flow-rate, 0.5 ml/min; wavelength, 200 nm. Order of elution: Cl^- or other impurity (a) 2.13 min, NO_3^- (b) 2.66 min, NO_2^- (c) 11.37 min.

$\text{NO}_3^-/\text{NO}_2^-$ in the environmental sciences, we have investigated possible interference by other easily dissociated anions (e.g., Cl^-): none was observed. Indeed, hydrochloric acid is eluted with the solvent front, as expected for an entirely dissociated acid. At this stage of investigation, the column appears selective for nitrate and nitrite ions, as shown by the comparative analysis carried out on a water sample collected in our campus, reported in Table 1. Aromatic acids are eluted in the column dead volume.

Current techniques employed to separate and to detect these compounds are generally based on a complex sequence of chemical reactions [7–9] or sophisticated – and time-consuming – capillary zone electrophoresis techniques [10]. Indeed, the need for a technique requiring a minimum of pretreatment for detecting both ions has often been underlined in the literature. Furthermore, the acidity of mordenite can be modulated over a wide range by varying the Si/Al ratio, making further application of this class of materials in ion-exclusion chromatography attractive. We thus suggest that this porous solid be utilised in ion-exchange chromatography when high ion-exchange capacity is not required and where further improvement of separation can be obtained by

Table 1
Comparative analysis of water

	NO ₃ ⁻ (mg/l)	NO ₂ ⁻ (µg/l)
Chemical analysis	7.2	10
Ion-exclusion chromatography on mordenite	7.0	11

modulating the acidity of the support. Last, but not least, we underline that the proposed material is much cheaper than current commercial macro-porous sulphonated styrene–divinylbenzene copolymer columns.

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