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Simultaneous determination of borate, chloride and molybdate in pyrohydrolysis distillates of plant and soil samples by ion chromatography

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ABSTRACT

Determination of concentrations of micronutrients in plant samples is important in order to assess the growth and quality of plants. An ion chromatography (IC) method was developed for the simultaneous determination of B, Cl and Mo (micronutrients present in their anionic form in aqueous samples) using a gradient elution with D-mannitol and NaOH. Despite their different chemical nature, these elements could be separated from the matrix by employing pyrohydrolysis. IC was employed for their sequential determination from single aliquot injection into the IC column. It was observed that the optimised procedures developed earlier in our laboratory for the separation of B and halogens using D-Mannitol-NaOH or bicarbonate eluents could not be extended to B-Mo-Cl separation. The concentration levels of D-mannitol in the eluent required for separation of boron impeded the conductivity detection of Mo and the peak sensitivity was seen to be critically dependent on D-mannitol concentration in the eluent. In addition, D-mannitol in NaOH eluent altered the retention times of analytes (B^- , Cl^- , NO_3^- , SO_4^{2-} and MoO_4^{2-}) which were not observed in the case of bicarbonate eluent. The current study deals with the investigation on the influence of D-mannitol on the molybdate as well as its role on the retention time. Formation of Mo-mannitol complex at different pH conditions and de-protonation of mannitol were correlated to the observed effects. Based on the observations, a gradient elution method was proposed for the simultaneous separation and determination of B, Cl and Mo in the pyrohydrolysis distillates of plant samples. The method was calibrated for B (0.05–1 mg/L), Cl (0.1–10 mg/L) and Mo (0.5–10 mg/L) and the linear regression coefficients obtained were 0.9992, 0.9998 and 0.997 respectively. The limit of detection (LOD) for B, Cl and Mo was calculated to be 19, 23 and 96 $\mu\text{g/L}$, respectively. The developed IC method after pyrohydrolytic separation of B, Cl and Mo was successfully applied for the analysis of real samples.

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1. Introduction

Boron, chlorine and molybdenum are important micronutrients for plants [1]. Boron plays an important role in the nuclear metabolism, photosynthesis, cellular differentiation, development etc. Chlorine is essential for osmosis and maintains cell charges [2]. Mo controls the enzyme function and is also essential for nitrogen fixation. On the other hand these elements can become toxic to the plants at higher concentrations. Since the plants obtain the

micronutrients through soil, quantification of these elements in plant and soil samples is useful for various physiological studies relevant to plant growth and crop yield [3–6]. Various analytical methods are available for the analysis of micronutrients in plant and soil samples, many of them are selective to an element or a group of elements having similar properties [7]. These methods follow an initial extraction of the analytes into a suitable medium followed by their determination [8]. Therefore, these methods may not be amenable for simultaneous analysis of elements of different chemical nature such as B, Mo and Cl. Simultaneous determination of boron, chlorine and molybdenum is advantageous; however, differences in their chemical properties make it a difficult task. For instance, a method often used for the separation of boron from the plant samples uses hydrochloric acid [9] and hence, the prepared

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sample cannot be used for the determination of chlorine. Similarly separation of Mo involves the use of several reagents which adds impurities in significant concentrations and therefore, the sample is unsuitable for carrying out the determination of boron and chlorine. Determination of chlorine is being carried out by extracting chloride from the plant samples using distilled water or distilled water and ranex-30 solution in which the complete extraction of boron and Mo is not realised [9]. Since these methods use concentrated acids and/or organic reagents, they are not amenable to ion chromatography analyses [9,10].

Pyrohydrolysis is a simple separation technique widely employed for separating boron and halides directly from several solid matrices. During pyrohydrolysis, the sample (solid matrix) is heated to 1173–1473 K in presence of a carrier gas (often oxygen) carrying steam and at this temperature; the volatile oxides of boron and halogens are formed. The formed species are transported through moist carrier gas which is condensed to form a distillate. The separated species are trapped in a dilute NaOH solution. The sample solution obtained from pyrohydrolysis is amenable to ion chromatographic analysis at trace level concentrations since it is free from the chemical reagents (except for the dilute NaOH trapping medium). Many analytical methods based on the combination of pyrohydrolysis (PH) and ion chromatography (IC) have been reported for the analysis of trace constituents in solid matrices [11]. PH and IC combination has been used for analysis of several carbon materials such as coals, graphite and paraffin wax [12–14]. Pyrohydrolytic separation of bromine and iodine from carbon nano tubes followed by their determination employing ICP-MS has also been reported [15]. Hence, it would be feasible to accomplish the pyrohydrolysis of plant samples. Many studies have been reported on the pyrohydrolytic separation of boron and halogens from different matrices [16–18]. Feasibility of separating molybdenum as molybdate ion employing pyrohydrolysis has been reported recently [19]. Subsequently the feasibility of separating B, F and Cl directly from a solid matrix as borate, fluoride and chloride simultaneously was also reported [18,20]. Since the individual pyrohydrolytic separations of boron as boric acid, chlorine as hydrochloric acid and Mo as $\text{MoO}_3 \cdot \text{H}_2\text{O}$ are accomplished in the temperature range between 1173 K and 1473 K, there is a scope for separating boron, chlorine and molybdenum simultaneously by using pyrohydrolysis.

Ion chromatography is a powerful analytical tool, which offers simultaneous separation as well as quantification of ionic species at trace level concentrations. Many applications on the ion chromatographic determination of common anions and cations such as nitrate, chloride, sulphate, phosphate, alkali and alkaline earth metal ions etc. in plant extracts have been reported [21–23]. For the determination of B, since boric acid is a weak acid, it is converted into either tetrafluoroborate [24] or mannitol-boric acid complex by adding D-mannitol [25]. Molybdenum has been determined as molybdate ion in different environmental samples [26,27].

For separating anions by ion chromatography with suppressed conductivity, carbonate, bicarbonate and hydroxide eluents are widely used. Hydroxide eluents are preferred over carbonates as they offer better sensitivity in suppressed conductivity detection, however, it has a limitation that it cannot be used with samples containing significant amount of metallic analytes as their hydroxide formation affects the column separation as well as the performance of the suppressor. Since pyrohydrolysis separates the analytes selectively, the concentration of metallic species in the sample solution is insignificant and therefore, it is highly compatible with the hydroxide eluents.

It is obvious that among the plant micronutrients, the separation and determination of B, Cl and Mo were carried out by independent methods due to the difficulties associated with their simultaneous separation. However, pyrohydrolysis is capable of separating B, Cl and Mo simultaneously and is advantageous over the tedious time

consuming independent separation methods. Although the sample solution prepared by pyrohydrolysis is amenable for ion chromatographic analysis as it provides the analytes, B, Cl and Mo in their anionic form in aqueous medium, their simultaneous IC separation and determination is not explored so far. The present study is aimed at developing a simple ion chromatographic method for the simultaneous determination of B, Cl and Mo in plant samples after their separation using pyrohydrolysis.

2. Experimental

2.1. Reagents and materials

Standard solutions of F^- , Cl^- , NO_3^- and SO_4^{2-} were prepared by dissolving their respective sodium salts of 99.9% purity (Merck). Standard solutions of MoO_4^{2-} were prepared by dissolving $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (99.98% pure, Sigma-Aldrich) whereas boric acid (99.99%, Merck) was used to prepare standard boron solution. Eluents were prepared by using GR grade NaOH, d(-)-mannitol, NaHCO_3 . All the solutions were prepared in high purity deionised water (18.2 M Ω .cm) obtained from a Milli-Q water system (Millipore).

2.2. Instrumentation

Pyrohydrolysis was carried out in an indigenously designed apparatus completely made up of quartz [28], which consists of a furnace, two concentric tubes viz. inner and outer tubes, a condenser and a sample collector containing a trapping solution. The sample loaded on a quartz boat is placed inside the inner tube and covered by the outer tube. The one end of the outer tube that contains the sample boat is placed inside the furnace whereas the other end is connected to a Liebig condenser.

The ion chromatograph system (Dionex, Model ICS-5000) consisting of a gradient pump, a suppressed conductivity detector (ED50A) equipped with an anion self-regenerator suppressor (ASRS-II) and a Rheodyne injector was used. Samples were introduced through a 50 μL loop fitted with the injector. IC separations were carried out on analytical separator columns, Waters make IC-Pak anion, (4.6 \times 50 mm, capacity: 30 $\mu\text{eq/mL}$, polymethacrylate resin with quaternary ammonium functional group), and Dionex make, IonPac AS18, (4 \times 250 mm, capacity: 285 μeq , ethylvinylbenzene/divinylbenzene functionalised with alkanol quaternary ammonium ion).

2.3. Samples and sample pre-treatment

Samples were obtained from rice plants grown in experimental gamma fields at Trombay and soil from the same fields. The root, leave, and shoot of plant samples were segregated and each part was dried at 353 K for 48 h in oven to remove the moisture. The dried plant parts were crushed in a mortar and pastel. Similarly the soil samples were also dried and ground to obtain small and homogeneous particles. Accurately weighed samples were taken in a quartz boat and subjected to pyrohydrolysis.

3. Results

3.1. IC separation of chloride, borate and molybdate along with common anions

3.1.1. Separation with bicarbonate eluent

For the separation of boron as borate ion on an anion exchange column, conversion of boric acid into boric acid-mannitol anionic complex is necessary. The formation of the complex and the sep-

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