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Short communication

Analysis of nerve agent degradation products using capillary ion electrophoresis

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Abstract

A method has been developed for the analysis of nerve agent degradation products using capillary ion electrophoresis. Analysis of the primary degradation products isopropyl methylphosphonic acid, ethyl methylphosphonic acid, pinacolyl methylphosphonic acid and methylphosphonic acid was accomplished with run times of less than 5 min. Detection of low mg/l levels of degradation products in spiked water samples was possible. Little sample preparation was required for the analysis of the alkyl methylphosphonic acids.

1. Introduction

With the end of the cold war military bases throughout the USA and elsewhere are being closed. Those bases that contained or stored chemical nerve agents must be identified, monitored and, if necessary, remediated. Those bases that currently store or destroy chemical munitions must also be monitored for possible contamination. Once exposed to the environment most chemical nerve agents readily degrade by hydrolysis to form alkyl methylphosphonic acids. Fig. 1 shows the breakdown process of each nerve agent [1]. The first hydrolysis is rapid and each particular alkyl methylphosphonic acid formed is particular to each originating nerve agent. While there are no current US Environmental Protection Agency regulations for these nerve agent degradation products, there are several military methods which describe the analysis of these compounds [1,2]. Most of these methods describe the use on ion chromatography for analysis. Using ion chromatography, low mg/l to mid ng/l levels of detection can be easily obtained [1,2]. Some of these methods require the use of a silver resin for chloride removal prior to analysis. This is because several of the compounds of interest elute near the chloride peak thus making identification and quantitation difficult if the chloride is not removed. Typical analysis times by ion chromatography for these alkyl methylphosphonic acids is 14 min or longer. Capillary ion electrophoresis (CIE) has been previously shown to be a fast and reliable technique for ion analysis [3–8]. CIE was applied to the analysis of these acids since the separation technique is different from ion chromatography and may provide better resolution or selectivity than ion chromatography. A chromate, high-mobility, electrolyte with an osmotic flow modifier (OFM) was used to separate the alkyl phosphonic acids. OFM is added to the elec-

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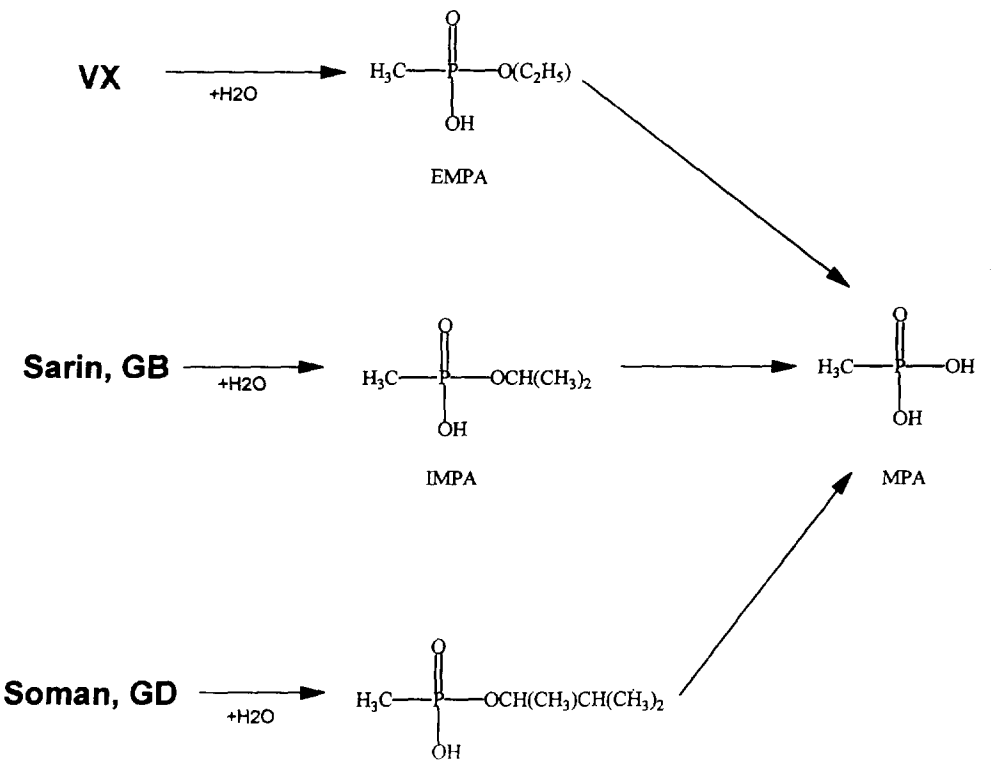

Fig. 1. Nerve agent degradation pathway for the three main alkyl methylphosphonic acids studied.

trolyte as an additive that reverses the normally cathodic direction of the electroosmotic flow (EOF) that is found in fused-silica capillaries. This creates a co-electroosmotic condition that augments the mobility of the analytes. To reduce excess carbonate typically found in the water samples, a Milli-Trap H^+ cartridge was used to reduce the carbonate. Analysis of the four main phosphonic acids was done in a spiked groundwater sample.

2. Experimental

2.1. Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta 4000E CIA (Waters, Milford, MA, USA). A Hg lamp was used for indirect UV detection at 254 nm. AccuSep polyimide fused-silica capillaries of 60 cm × 75 μm I.D. were used throughout.

Data acquisition was carried out with a Waters Millennium 2010 Chromatography Manager with a SAT/IN module connecting the CE system to the data station with the signal polarity inverted from the CE system. Detector time constant for the CE was set at 0.1 s for anion analysis The data rate for the CE was 20 points/s. Collection of electropherographic data was initiated by a signal connection between the CE system and the SAT/IN module.

2.2. Chemicals and sample treatment

The chromate electrolyte was prepared from a concentrate containing 100 m*M* Na_2CrO_4 (Fisher Scientific, Pittsburgh, PA, USA) and

0.017 m*M* H_2SO_4 (Fisher Scientific Ultrex Grade). Milli-Q reagent-grade water (Millipore, Bedford, MA, USA) was used for all rinsing, dilution and preparation. OFM was obtained in the Br form as a 20 m*M* concentrate from Waters [9]. Milli-Trap H^+ cartridges (Waters) were used for sample pretreatment of the ground- and tapwater samples. H^+ resin was obtained from Bio-Rad (Hercules, CA, USA) and converted to the Ag^+ form by soaking the resin for 24 h in a concentrated solution of $AgNO_3$. The resulting resin was packed in 3–5-ml slurries onto 10-ml syringes with disposable filters on the end of them and rinsed several times with high-purity water. Water samples were then passed through the resin and the effluent collected as well as a water blank. Standards of isopropyl methylphosphonic acid (IMPA), ethyl methylphosphonic acid (EMPA), pinacolyl methylphosphonic acid (PMPA) and methylphosphonic acid (MPA) were supplied by the US Army Environmental Center (USAEC). All other chemicals used were of ACS grade or better.

3. Results and discussion

Fig. 2 is an electropherogram of all four compounds of interest. The advantage of CIE is that these peaks elute after the main anions (i.e. chloride, sulfate, nitrate, etc.) that are found in most water samples and the analysis time is less than 5 min. The main peak prior to MPA at 2.7 min in Fig. 2 is carbonate. Prior to carbonate in the electropherogram fluoride and phosphate would migrate as well. These two peaks were found to almost coelute since the electrolyte pH had been raised, to allow for MPA to be resolved from carbonate, from the normal pH of 8 to a higher pH of approximately 9.2. Fig. 3A is an electropherogram of a spiked groundwater sample. The migration of MPA with carbonate is still

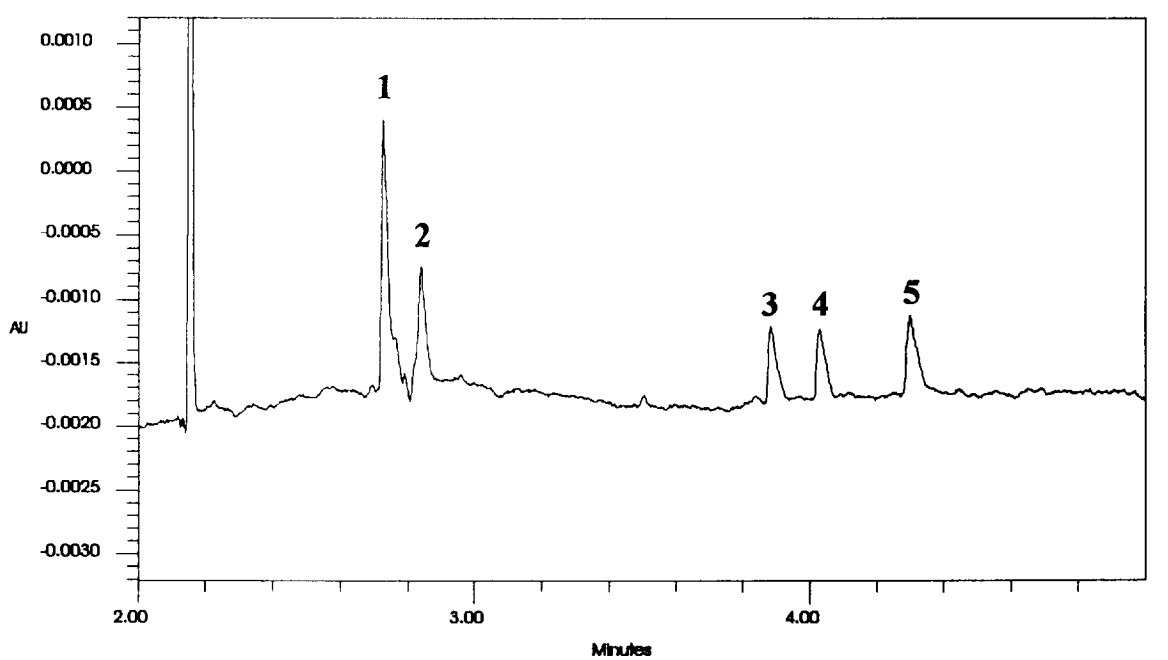

Fig. 2. Electropherogram of a standard. CIE conditions: fused-silica 60 cm × 75 μm I.D. capillary; voltage: 18 kV (negative); electrolyte: 4.5 m*M* chromate–0.5 m*M* OFM–1.0 m*M* $NaHCO_3$; indirect UV detection at 254 nm; hydrostatic injecton (10 cm for 30 s). Peaks: 1 = carbonate (8.0 mg/l); 2 = MPA (7.0 mg/l); 3 = EMPA (3.1 mg/l); 4 = IMPA (3.3 mg/l); 5 = PMPA (3.3 mg/l).

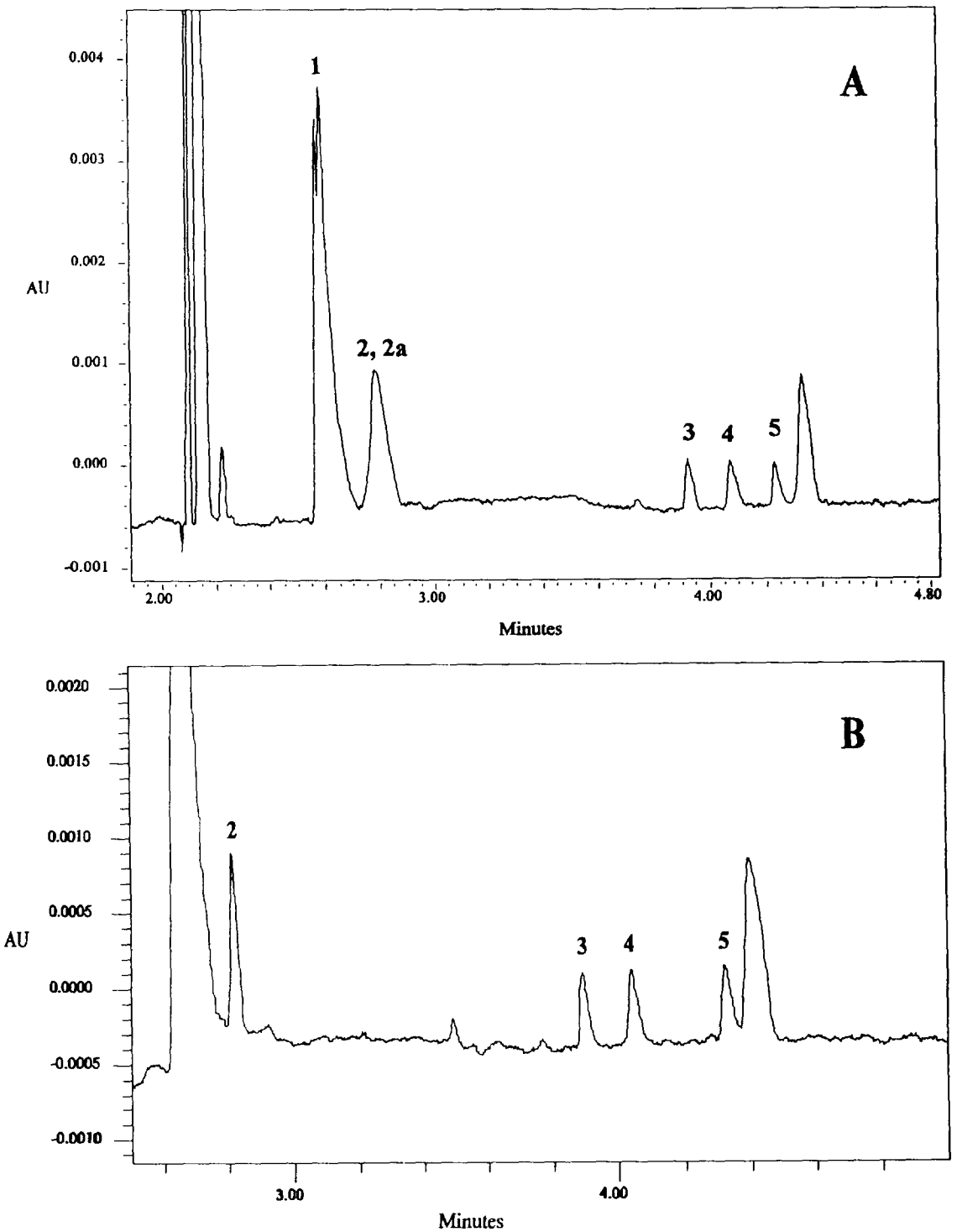

Fig. 3. Electropherogram of spiked groundwater sample without (A) and with (B) passing it through a Milli-Trap H^+ cartridge. Peaks: 1 = fluoride and hydrogen phosphate; 2 = MPA (7.1 mg/l); 2a = carbonate (natural levels); 3 = EMPA (3.1 mg/l); 4 = IMPA (3.3 mg/l); 5 = PMPA (3.3 mg/l). Conditions as in Fig. 1.

an issue, especially in groundwater samples that contain high carbonate levels as is the case with the sample in Fig. 3. One solution was to run the samples through a Milli-Trap H^+ cartridge which removes any excess carbonate from the sample without effecting the remaining ions. Milli-Trap H^+ cartridges have been described and used previously for carbonate removal from groundwater samples prior to ion chromatographic analysis [10,11]. Fig. 3B is the same spiked groundwater sample except that it had been passed through a Milli-Trap cartridge. MPA is now resolved (Fig. 3B) and the peak just prior to it is fluoride and hydrogenphosphate.

In the case of samples containing very high chloride levels sample pretreatment by passing the water through an Ag^+ resin, just like for ion chromatographic analysis, can be done as well.

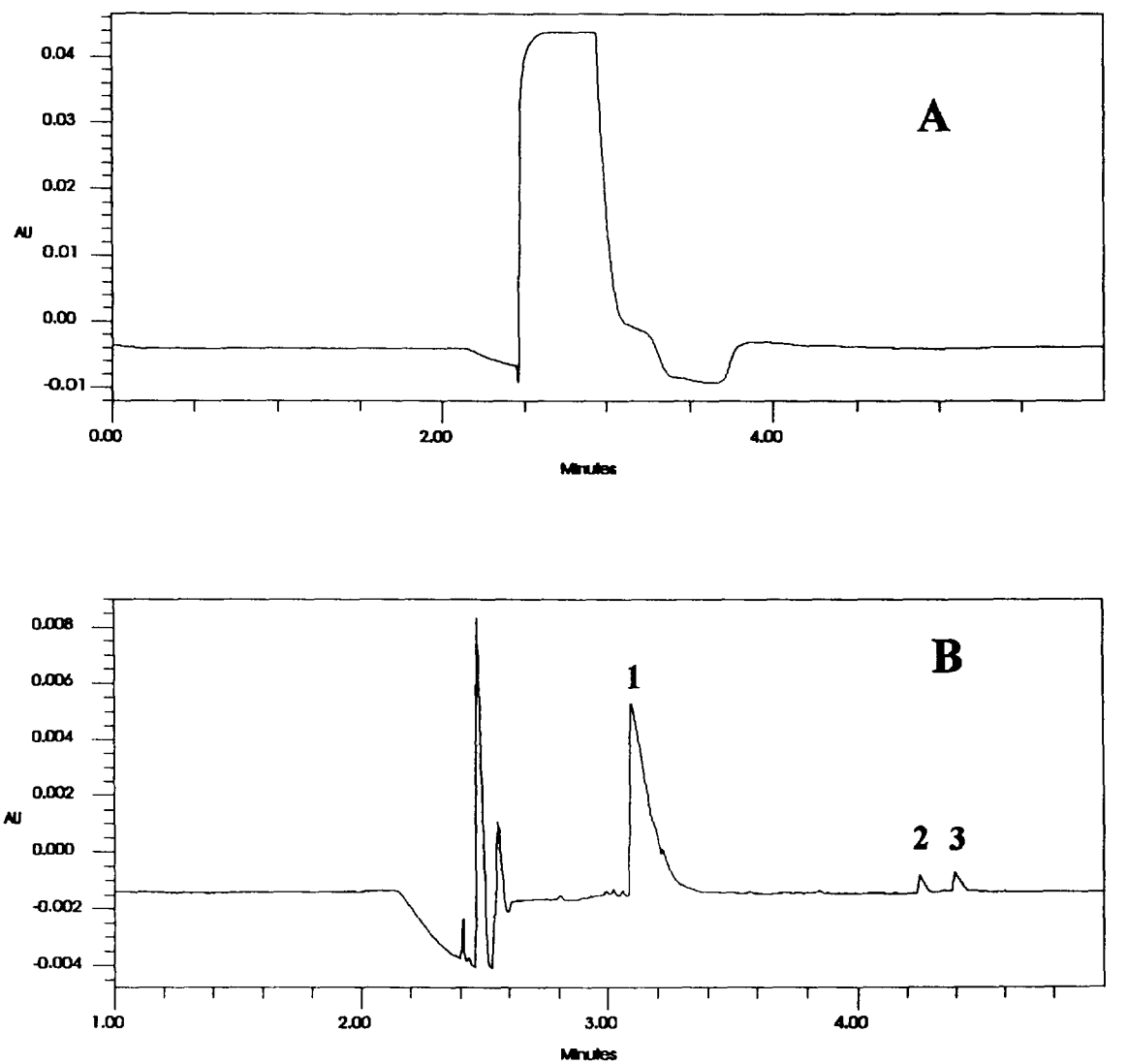

Fig. 4. Electropherogram of the spiked water sample containing a high level of chloride (approximately 4000 mg/l) before (A) and after (B) pretreatment with the Ag^+ resin. Peaks: 1 = fluoride/phosphate and carbonate (natural levels); 2 = EMPA; 3 = IMPA. Conditions as in Fig. 1.

Fig. 4A is an example of a spiked water sample containing over 4000 mg/l of chloride with IMPA and EMPA spiked in at levels of approximately 7.0 mg/l. Fig. 4A is the spiked groundwater sample without any pretreatment, and Fig. 4B is the same sample after passing the water sample through the Ag^+ resin. As can be seen in Fig. 4B the high chloride level has been reduced now allowing for EMPA and IMPA to be resolved.

CIE offers the potential for analysis of these main alkyl methylphosphonic acids with analysis times of less than 5 min. Further, the use of a silver resin and the Milli-Trap cartridge for sample pretreatment offers the potential for reducing interfering ions from the sample prior to analysis.

4. Further work

Further work on improving this method will continue, especially in the area of MPA detection. One area of interest is in using electromigration as an injection technique. This offers the ability to preconcentrate ions on the head of the capillary. Another are of interest is in other electrolytes which may mask the carbonate completely allowing for easier MPA identification and quantitation.

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