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Rapid estimation of trace organophosphonate used as a scale inhibitor in aqueous systems by reactive pyrolysis-gas chromatography/mass spectrometry

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ABSTRACT

The determination of trace organophosphonates which are used in cooling towers as a scale inhibitor usually involves extraction and/or concentration of the target components prior to analysis. The extracts are analyzed using chromatographic or spectroscopic methods. This methodology is not only cumbersome but also results in poor data quality. This work presents a novel approach for the rapid and sensitive determination of trace amounts of an organophosphonate: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) in aqueous solution. This method is based upon reactive pyrolysis-GC/MS in the presence of tetramethyl ammonium hydroxide (TMAH). Approximately 10 μL of the aqueous sample containing a trace amount of HEDP and 1 μL of 25% a methanol TMAH solution was placed in the sample cup. The cup was then dropped into the furnace which was at 350 °C. The heat initiated the hydrolysis of the organophosphonate followed by the methylation of the hydrolysates. Trimethylphosphate (TMP) was detected by GC/MS. The level of TMP is related to the level of the phosphonate, HEDP in the aqueous sample. Using an external standard calibration curve, it was possible to make a rapid estimation of mg/L levels of organophosphate.

1. Introduction

Organophosphonates such as 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) are used in a variety of applications such as industrial water treatment, household and industrial surfactants, pulp and paper processing, oil recovery operations, etc. The determination of trace organophosphonates in water usually involves extraction and/or concentration of the target components prior to analysis. The extracts have been analyzed using various analytical methods such as ion chromatography, capillary electrophoresis, spectrophotometry, atomic absorption spectrometry, atomic emission spectrometry, etc. [1,2]. These conventional methodologies are not only cumbersome in pretreatments but also result in poor data quality. Atomic spectroscopic methods are the widely used and they only provide total phosphorous content in a given aqueous sample system and not speciated organophosphonate content. There is interest in a rapid, sensitive and definitive method to determine trace amounts of organophosphonates in aqueous systems.

The application of modern analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is rapidly expanding beyond basic polymer chemistry [3–10] into fields as diverse as biochemistry, geochemistry, forensic science, food science, toxicology, and polymer recycling. In addition, reactive pyrolysis techniques using primarily tetramethylammonium hydroxide (TMAH) $[(CH_3)_4NOH]$ often provide specific information on the chemical structure of various organic materials that is not readily obtainable by conventional pyrolysis methods [11,12]. Reactive pyrolysis has been primarily applied to the characterization of organic materials such as polyesters and polycarbonates, and organic compounds such as lipids and fatty acids, etc. [13–16].

In this work, reactive pyrolysis using an organic alkali, was used to develop a new analytical method for trace HEDP. The sample is analyzed directly, that is, without using any preliminary sample treatments.

2. Experimental

2.1. Materials

A water solution containing 60 wt% of 1-hydroxyethylidene-1,1-diphosphonic acid(HEDP) $[CH_3C(OH)(PO_3H_2)_2]$ was obtained from

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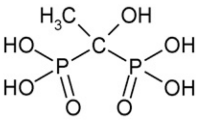

Fig. 1. Molecular structure of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP).

Thermphos Trading (Netherlands). The chemical structure of HEDP is shown in Fig. 1.

Four aqueous solutions containing 1, 10, 100 and 1000 mg/L of HEDP were prepared and served as test samples for the reactive pyrolysis measurements.

A methanol solution of tetramethylammonium hydroxide (TMAH) [$(CH_3)_4NOH$] supplied by Aldrich Chemical Company Inc., was used as the reagent for the reactive pyrolysis.

2.2. Conditions for reactive pyrolysis-GC/MS measurements

Fig. 2a illustrates the chromatographic system used for the reactive pyrolysis-GC/MS. A vertical, micro furnace pyrolyzer (PY-2020iD, Frontier-Lab, Japan) was used to rapidly heat the sample to 350 °C. The pyrolyzer was interfaced to the GC via a split injector, and the separation column was interfaced directly to the electron ionization (EI) source (Agilent 5973A, Santa Clara, CA, USA).

The procedure used to prepare the sample for analysis is shown in Fig. 2b. Approximately 10 μL of the sample solution and 1 μL of the TMAH methanol solution were injected into the sample cup, which was then suspended, at ambient temperature and in a helium atmosphere, in the "hold" position of the pyrolyzer. The reagent amount contained in the 1 μL of TMAH methanol solution is more than 100 times the stoichiometric value needed to react with the organophosphonate contained in 10 μL of the 0.01 wt% solution. The sample cup was dropped into the center of the furnace which was at 350 °C; the reaction pyrolysis took place in a helium atmosphere. The He carrier gas flow was 50 mL/min. The components thermochemically formed in the pyrolyzer were dynamically transferred to the separation column. The smaller portion of the flow (1 mL out of 50 mL) was transferred to the column through a splitter. The HEDP reaction products are separated using a stainless steel capillary column (Ultra ALLOY-5, Frontier-Lab; length: 30 m, I.D.: 0.25 mm, thickness: 1 μm, stationary phase: 5% diphenyl 95% dimethyl-polysiloxane). The GC oven temperature was programmed from 60 to 200 °C at 20 °C/min and then maintained for 3 min.

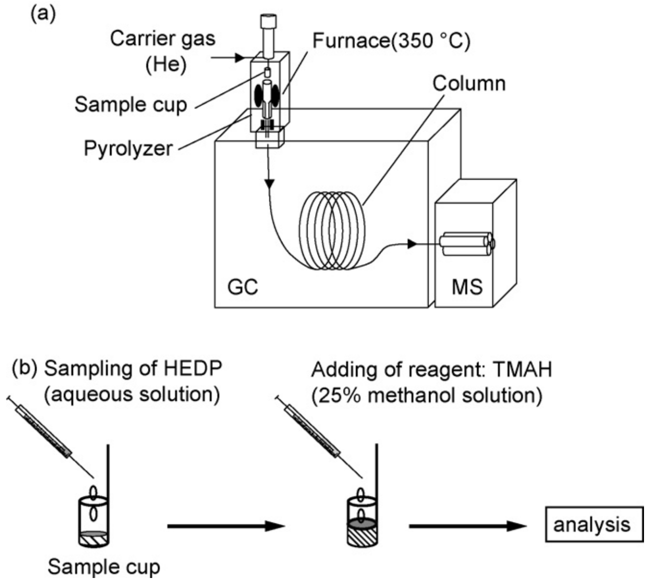

Fig. 2. (a) Schematic diagram of the reactive pyrolysis-GC/MS system. (b) Preparation of the sample for reactive pyrolysis-GC/MS.

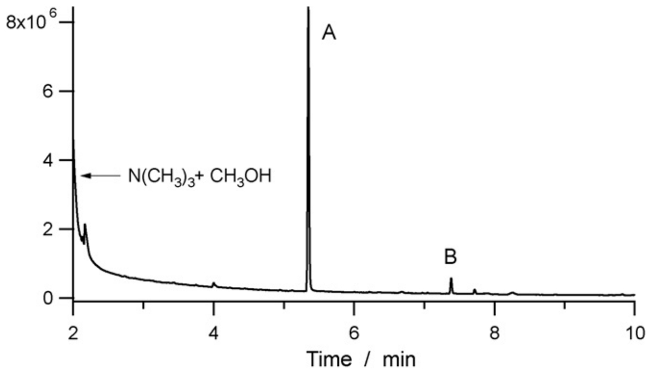

Fig. 3. Total ion chromatogram resulting from the reactive pyrolysis of trace-level HEDP in water.

The chromatographic measurements were carried out either by total ion current (TIC) between 29 and 600 m/z or single ion monitoring (SIM) at a fixed mass-to-charge ratio. Identification of the characteristic peaks on the resulting chromatograms was based on their EI mass spectra by using the NIST (National Institute of Standards and Technology) mass spectral library search Ver.2.0 (NIST 08, NIST, Gaithersburg, MD, USA).

3. Results and discussion

Fig. 3 shows a total ion chromatogram (TIC) obtained after the reactive pyrolysis of HEDP (1000 mg/L) in an aqueous solution. After the elution of the two large methanol and trimethylammonium peaks which originate from the excess TMAH reagent, a prominent peak was observed at ca. 5.4 min (A) together with a minor one at 7.4 min (B). The observed mass spectra for peak A and peak B are shown in Fig. 4. According to the mass spectrum for peak A with M^+ at $m/z = 140$ and $[M-2CH_3]^+$ at $m/z = 110$, it was identified as a

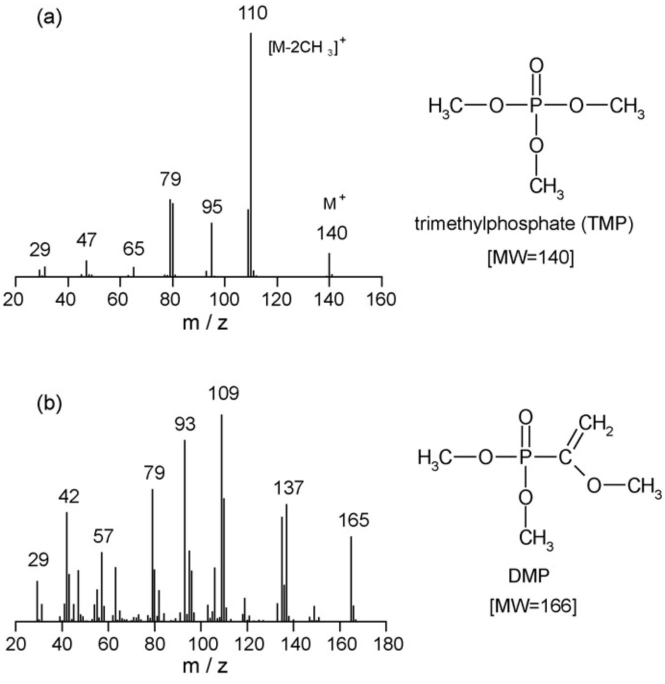

Fig. 4. The mass spectra of peak A (a) and peak B (b) on the total ion chromatogram in Fig. 3 and corresponding molecular structure of the identified compounds.