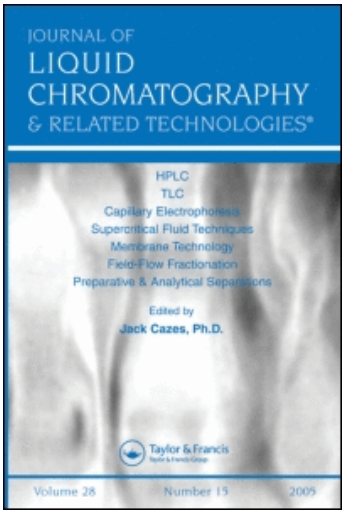

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DETERMINATION OF CARBOXYLIC ACIDS IN WATER-SOLUBLE POLYACRYLATES BY MICELLAR ELECTROKINETIC CAPILLARY ELECTROPHORESIS WITH INDIRECT DETECTION

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ABSTRACT

A micellar electrokinetic capillary electrophoresis method employing indirect detection was developed to separate and quantify mercaptoacetic acid (thioglycolic acid), acrylic acid (2-propenoic acid), methacrylic acid (2-methylpropenoic acid), mercaptopropionic acid, and the dimer of mercaptopropionic acid in water-soluble polyacrylates. Samples are extracted in water and quantitation is performed by indirect UV photodiode array detection at 340 nm with a reference of 210 nm. Samples are obtained from industrial plant processes and analyzed for all compounds by capillary electrophoresis (CE).

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INTRODUCTION

The use of capillary electrophoresis as an analytical tool in laboratories has increased dramatically over the years but is still limited in certain areas, such as industrial applications. CE is a separation technique that offers numerous advantages such as high efficiency, small sample volumes, and operation in an aqueous media. It is also able to operate in numerous modes such as micellar electrokinetic chromatography (MEKC) and capillary electrochromatography (CEC). One of the drawbacks of CE is the decreased sensitivity due to on-line detection, but in many cases this is not an issue due to high analyte concentrations. Unfortunately, CE also has the perception of lacking reproducibility. With proper capillary conditioning and buffer replenishment, however, reproducible results can be achieved, especially if using a reference peak to account for migration time variations. It is also crucial to pay particular attention to buffer preparation since a small change in concentration and pH can lead to drastic changes in overall separation.

In conventional CE methods the polarity (or power supply) is positive. With positive polarity the inlet is designated as the anode and the outlet the cathode. This will cause the electro-osmotic flow (EOF) to flow in the direction of the cathode, creating an order of migration of cations, neutrals, and finally anionic species. In this method, the EOF is reversed by the addition of a cationic surfactant, cetyltrimethylammonium bromide (CTAB). The surfactant is absorbed onto the capillary wall due to electrostatic attraction between the positively charged ammonium in the CTAB and the negatively charged Si-O groups of the fused silica capillary.[1]

If the surfactant concentration is high enough the hydrophobic tails of the surfactant will form a bilayer. This creates a charge reversal on the fused silica capillary from a negative to positive charge, since the cationic head groups of the surfactant are orientated towards the buffer. This leads to a reversal of the EOF, resulting in migration of the analytes from the cathode to the anode. With EOF reversal the power supply polarity needs to be reversed in order for analytes to flow past the detection cell. The order of migration will now be anions, neutrals, and cations.

This paper describes a MEKC method for the analysis of carboxylic acids contained in water-soluble polyacrylate additives. There are numerous separation methods for organic acids cited in the literature, mainly in the food industry, but few papers target industrial applications or the carboxylic acids investigated here. Volgger et al.[2] examined acrylic acid along with numerous aliphatic carboxylic acids in reaction broths of citric and itaconic acid in supercritical water by CE. Direct UV detection at 185 with a borate-phosphate electrolyte, as well as indirect detection with a background electrolyte of phthalic acid was examined. Giarrocco[3] examined impurities in acrylic acid and was able to separate acetic

acid, propionic acid, acrylic acid, 4-methoxyphenol, and the acrylic acid dimer by gas chromatography (GC). Chen[4] determined organic acids in industrial streams by ion chromatography following a solid phase extraction step. The method was later improved using capillary electrophoresis combined with an aqueous extraction.[5]

Hesse et al.[6] developed a method for determining inorganics and mercapto compounds in lime liquor using ion chromatography. Similarly, Ohnuki et al.[7] and Wygant[8] developed methods for analyzing mercaptoacetic acid and other ingredients in personal care products using capillary electrophoresis and ion chromatography, respectively. Neyer et. al.[9] determined acrylic acid in incontinence products containing polyacrylic gelling agents by HPLC and ion exclusion HPLC. In these methods and others,[10-13] the procedures involved complex derivatization of the analytes and the use of various experimental conditions. Ridder et al. used CE to determine the response of biotrickling filters to sudden loads of methylmethacrylate (MMA) by measuring the levels of methacrylic acid, a degradation product of MMA.[14] Other methods for methacrylic acid include gas chromatography (GC) with FID detectors[15] and high performance liquid chromatography (HPLC).[16]

Organic acids are typically the oxidation or degradation products of various organic molecules and can be found in a variety of organic reaction mixtures. Their identification and quantitation are crucial for proper product development. Acrylic acid (Fig. 1) is the simplest organic acid that contains a carbon-carbon double bond. It is used to form acrylate compounds and is a highly reactive mol-

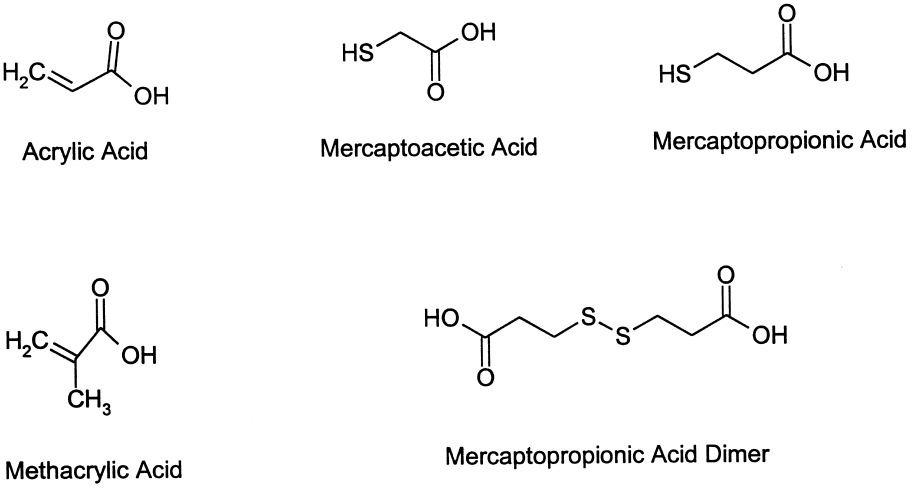

Figure 1. Chemical structures of various carboxylic acids found in polyacrylate additives.

ecule that readily undergoes polymerization and esterification reactions. The acrylates created are used in a wide array of products including coatings, and binders for leather and textile products. The polymers are used for the preparation of floor polishes and industrial coatings,[3] and are known for their water absorbing properties. Both mercaptoacetic and mercaptopropionic acids (Fig. 1) are commonly used in personal care products such as depilatory and hair waving preparations. Most acids are extremely toxic and can cause serious injury upon exposure at significant concentrations. Moreover, the acids possess disagreeable odors and fumes that could pose serious health hazards even when used under ideal circumstances. Most commercial materials that contain one or more of these acids are required to meet stringent product specifications. Thus, it is critical to be able to accurately quantitate levels of the acids using reliable analytical methodology.

The purpose of this work was to develop a simple and reliable method for the analysis of carboxylic acids in industrial polyacrylate materials using capillary electrophoresis. The analysis of mercaptoacetic, mercaptopropionic, acrylic acid, methacrylic acid, and mercaptopropionic acid dimer was achieved using a phthalate buffer and indirect UV detection.

EXPERIMENTAL

Apparatus

All chemicals used were analytical grade. Phthalic acid (99%) and cetyltrimethyl-ammonium bromide (CTAB, 99%) was purchased from ACROS (New Jersey, USA). Sodium hydroxide (50% w/w) was purchased from Scientific Equipment Co. (Aston, PA). HPLC grade methanol was purchased from Fisher-Scientific (Fair Lawn, New Jersey) and the 1.0 and 0.1 N sodium hydroxide solutions were purchased from Hewlett Packard. The standards used include mercaptoacetic acid, acrylic acid, mercaptopropionic acid, and the dimer of mercaptopropionic acid, all were obtained from in-house sources.

Standard Preparation

Stock standards of mercaptoacetic acid, acrylic acid, methacrylic acid, mercaptopropionic acid, and the dimer were prepared by accurately weighing 0.1 g of each component and bringing up to volume with methanol in a 100 mL volumetric flask. Working standards were then prepared by making appropriate dilutions from the stock standard into HPLC grade water. Working standards for mercaptoacetic acid need to be prepared daily due to degradation.

Buffer Preparation

A 50 mM phthalate buffer concentrate was prepared by dissolving 4.1285 g phthalic acid in 25 mL methanol in a 500 mL volumetric flask. Then, 40 mL of 1.0 N NaOH was added and brought to a final volume of 400 mL with HPLC grade water. The CTAB (0.4755 g) was then added to the flask and allowed to dissolve. The pH was adjusted to 7.0 using 1.0 N NaOH (approximately 6 mL). The final volume was then adjusted to 500 mL with HPLC grade water. For the analysis, 50 mL of the concentrate was added to a 500-mL volumetric flask and brought to volume with HPLC grade water. Prior to analysis, the buffer was filtered through a 0.2 μm filter disk.[5]

Sample Extraction

Samples were accurately weighed (0.3 g) and extracted using a specified volume of distilled, deionized water (18.3 MΩ cm resistance), obtained by treating distilled water using a Barnstead (Dubuque, IA, USA) Nanopure water purification system. The extracted samples were filtered and then transferred to individual vials for analysis by CE. Diluting samples with water helps to promote sample stacking.

CE Analysis

Quantitation of mercaptoacetic acid, acrylic acid, methacrylic, mercaptopropionic acid, and the mercaptopropionic acid dimer was performed on a Hewlett-Packard[3D] CE capillary electrophoresis system equipped with a photodiode array detector and an extended light path capillary (50 μM ID). At the start of each day the CE instrument was conditioned by flushing for 20 minutes with 1.0 M NaOH, 20 minutes with 0.1 M NaOH, and 40 minutes with running buffer. Prior to each injection, a replenishment and pre-conditioning step was employed. Pre-conditioning was performed by applying -20 kV for one minute followed by a 3-minute flush with 0.1 M NaOH and then a 5 minute flush with buffer. It is crucial that the flushing step does not involve the inlet and outlet buffer vials used for the sample analysis. A separate flush vial and waste vial need to be dedicated for the procedure.

The wavelength monitored was a detection wavelength of 340 nm and a reference wavelength of 210 nm for all compounds. The capillary column has an internal diameter of 50 μm ID, total length of 64.5 cm and an effective length of 56 cm. Capillaries of shorter length caused compounds to co-elute.

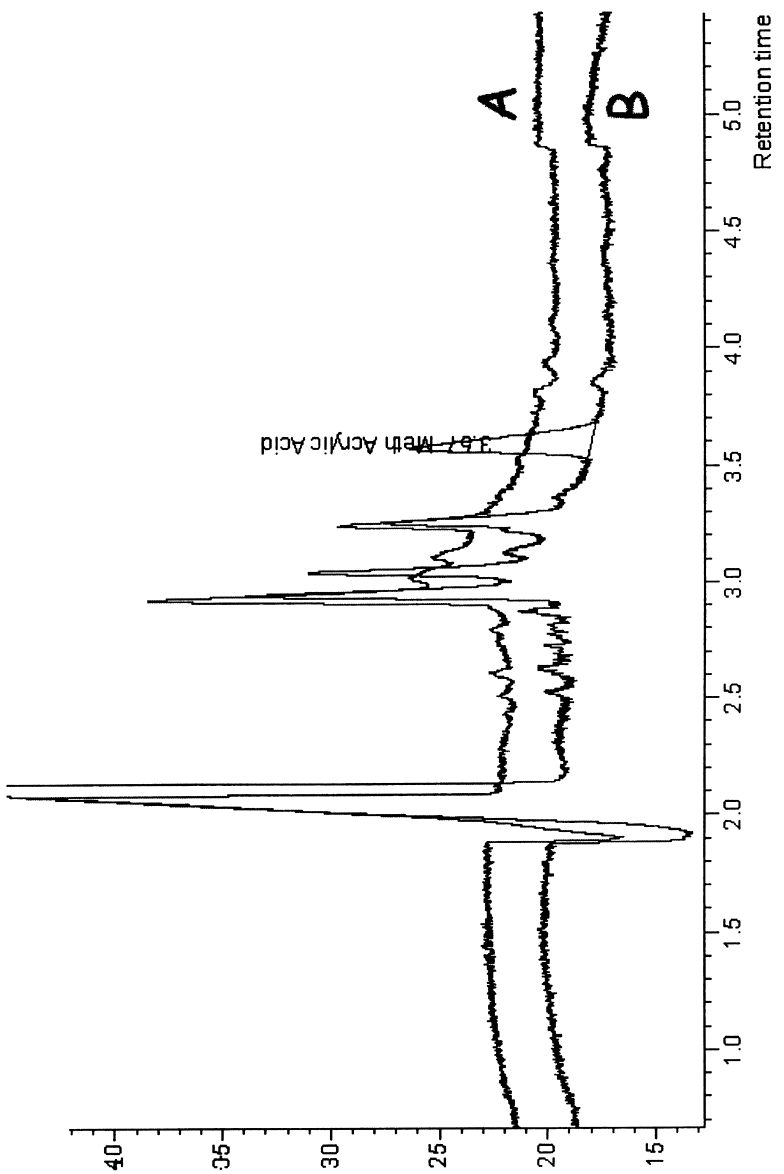

Figure 2. Electropherogram is a product with no methacrylic acid present. Trace B is a product found to contain methacrylic acid. (Conditions as described in text.)

Rinsing, sample introduction, and separation were all controlled by a HP Vectra XM2 with CHEMSTATION software. Sample introduction was performed hydrodynamically for 10 seconds at 50 mbar. The system was ramped from time 0 at 0 kV to -20 kV at 0.2 minutes. This allows the current to gradually ramp, eliminating the formation of bubbles within the capillary. The capillary temperature was maintained at 25°C and the sample carousel at 25.9°C.

Linearity Studies

From stock standards of mercapoacetic acid, acrylic acid, mercaptopropionic acid, and the mercaptopropionic acid dimer, various working standards were prepared for linearity testing. Mercaptopropionic acid was determined to be linear from 1 to 50 ppm with a coefficient of determination 0.99. The mercaptopropionic acid dimer was determined to be linear from 1 to 100 ppm with a coefficient of determination of 0.99. Both acrylic, methacrylic, and mercaptoacetic acids were linear from 1 to 100 ppm with coefficients of determination >0.99. For all components, the response was compared to peak area.

RESULTS AND DISCUSSION

Sample Preparation and Analysis

A fundamental constituent of CE analysis involves the generation of electroosmotic flow (EOF), which is created from the effect of an applied electric field on the solution double-layer formed at the inner surface of the capillary wall. The consistency of the EOF can often be disrupted when materials in the sample matrix bind to the inner surface of the capillary wall. Specifically, the presence of polymers in the sample matrix can serve to reduce the EOF through coating of the inner wall. Prolonged exposure of the inner surface of the capillary to this type of matrix can lead to irreproducible migration times and band dispersion. To minimize such effects on EOF in this work, samples were prepared using specific amounts of the polyacrylate additives (~ 0.3 g) in water (10 mL). The samples were also filtered and degassed prior to analysis using a 0.20 μm syringe membrane filter (Gellman, Ann Arbor, MI). Due to the unstable nature and susceptibility of the acids to oxidation and/or dimerization, the standards and samples were immediately analyzed upon preparation.

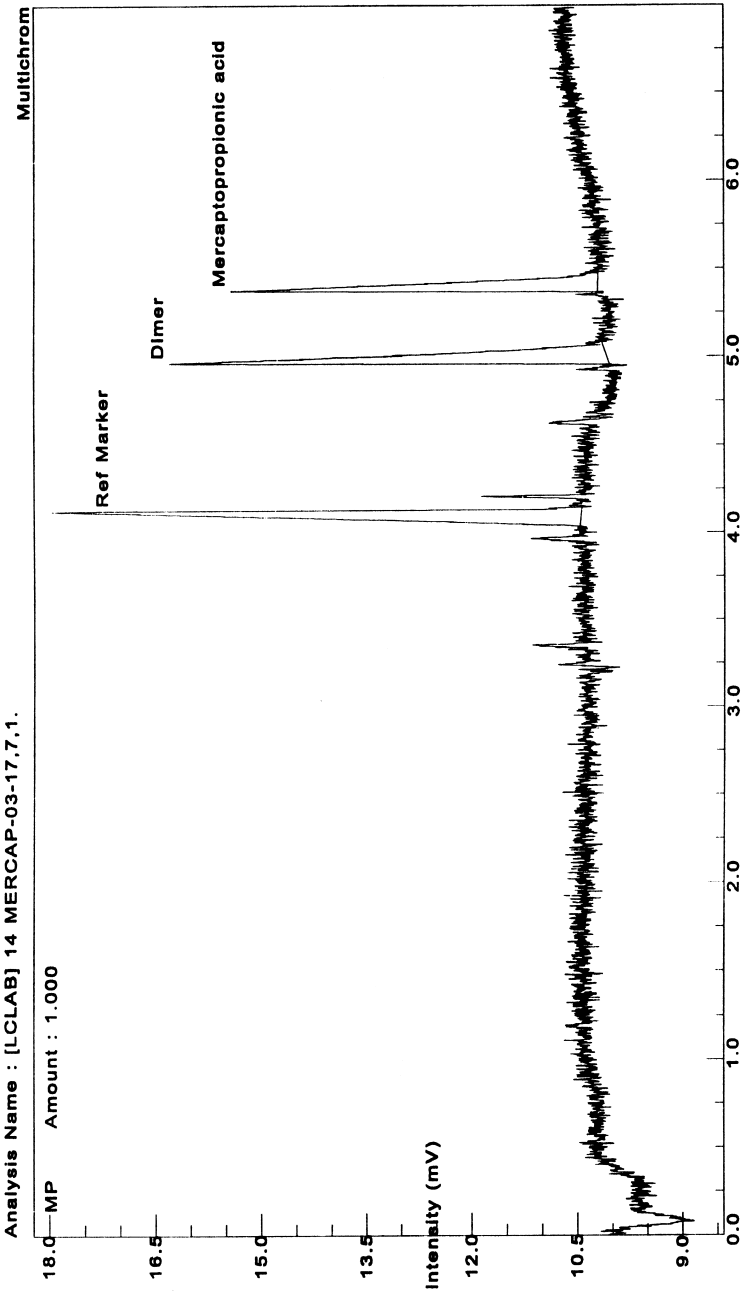

Figure 3. Electropherogram of the reference marker (maleic acid) with mercaptopropionic acid and its dimer. Conditions described in text.

Capillary Pre-conditioning and Buffer Replenishment

There are numerous factors involved in attaining good reproducibility in CE. One of the most important factors is proper capillary conditioning. This method uses a three step pre-conditioning process. The first was to apply a potential across the capillary to aid in cleaning the capillary inner surface. The base conditioning with NaOH removes adsorbing compounds and reconditions the silanol groups on the inner wall of the capillary. The last stage, a flush with buffer, re-equilibrates the surface of the capillary. Longer equilibration times with fresh buffer will lead to more stable migration times. Buffer replenishment prior to each injection is also needed to obtain stability in migration times. Without buffer replenishment electrolyte/buffer depletion may occur, which will adversely affect reproducibility.[12] Also, electrolysis of the buffer can cause changes in buffer composition and pH that will ultimately alter the EOF and migration times of compounds.

If migration times still vary then a compound can be added to the sample during preparation to determine the relative retention times. This is another way to identify peaks in conjunction with spectral data. It was found that with some samples the migration times shifted, this was most likely due to polyols adhering to the capillary surface. In this work, maleic acid was found to serve as an effective relative retention time marker. Figure 3 depicts an electropherogram of the reference marker (maleic acid) with mercaptopropionic acid and its dimer.

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