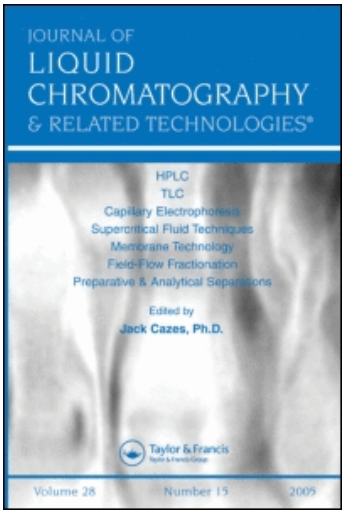

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THE DETECTION OF ORGANIC ACIDS IN A NON-OXIDATION MODE USING AN AMPEROMETRIC DETECTOR

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ABSTRACT

A group of organic acids including benzoic acid and oxalic acid along with sodium nitrate were determined using anion exchange columns and amperometric detection. The eluants used in the work were ortho-chlorobenzoic acid and phthalic acid. The response time was less than ten minutes and the detection limits were between 20 and 50 ppm. Both silver and platinum working electrodes were investigated and the response of the analytes to the amperometetric detector was a function of electrode material, applied voltage, eluant composition, and analyte. The nature of the detection mechanism is one involving the disruption of the electrode equilibrium and does not involve a true oxidation-reduction process.

INTRODUCTION

Ion chromatography is a powerful analytical tool for the separation of inorganic and organic ionic species(1). Most applications of ion chromatography make use of a general detection mode such as conductivity detection which responds to the general property of conduction which is

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exhibited by all ionic species (2,3,4). In certain cases, however, the use of a more specific detection mechanism, such as amperometric detection, is beneficial in that it can provide an improved detection ability for specific species. In general, the use of an amperometric detector has been limited to those species which can be either oxidized or reduced sufficiently well in water to provide an easily measureable current. Examples of the use of an amperometric detector include the determination of sulfide (5), the determination of cyanide (6), and the determination of iodide (7). More recent work using pulsed amperometric detectors has involved the determination of carbohydrates (8). The one thing which has been common in the above cited experiments is that the species of interest undergo an oxidation-reduction reaction at the electrode surface. A recent report indicated that the amperometric detector may also be capable of responding to species which do not undergo oxidation-reduction (9). Although the mode of action has not been fully delineated in the literature, possible mechanisms involve measurements involving changes in pH, changes in the electrode double layer with a consequent change in the current carrying ability of the electrode system, or a direct current conductance reading under non-equilibrium conditions. The work reported here is an extension of this non-redox mechanism in that fully oxidized species, organic acids as well the nitrate ion, can be determined using amperometric detection with reasonable detection limits.

MATERIALS

Chromatographic System.

The chromatographic system was composed of the following parts listed in order of occurrence in the flow path. The pump was a Kratos Spectroflow 400 Solvent Delivery System operated at 3.0 mL/min. A Kratos Spectroflow 480 Injection System was used to introduce 0.020 mL of sample into the system. The separator column was a Vydac 302IC4.6 anion exchange column. The detector was a Dionex Potentiostat amperometric Detector. (This is not a pulsed amperometric detector). Working electrodes were either silver or platinum. The output setting on the detector was 30nA/V with the applied potential varied between -0.20V and +1.0V for the platinum electrode and between 0.00V and +0.50V for the silver electrode. All chromatographic results were recorded on a Linear Instruments 1200 Chart Recorder.

Eluants

Two different eluants were used in this experiment. The main eluant was an orthochlorobenzoic eluant prepared by making a 0.001 M

orthochlorobenzoic acid solution, adding 150 mL of methanol to provide 1.00 L of eluant. The pH of this eluant was then adjusted to 4.00 using 1M NaOH. The second eluant was 0.001 M phthalic acid.

Reagents

The analyte species used in this experiment were benzoic acid, oxalic acid, phthalic acid, disodium EDTA, sodium nitrate and sodium sulfate. The solutions of the organic acids were prepared from the reagent grade pure compounds. The inorganic species were prepared from reagent grade salts. All analyte species were prepared at 100 ppm concentration using the orthochlorobenzoic acid eluant. Detection limits were determined by diluting the 100 ppm stock solution until a signal:noise ratio of approximately three was obtained experimentally.

Procedure

The following procedure was used in the experimental portion of this work. First, the platinum electrode was investigated using the orthochlorobenzoic acid eluant. Each of the analyte species was injected at -0.20V applied potential (versus the silver/silver chloride reference electrode). Then the potential was changed by 0.10V more positive and the solutions were re-injected. This was continued until a maximum potential of 1.0V was obtained. The optimum conditions were then determined by inspection of the chromatograms and the detection limits were determined at the optimum applied potential for each analyte species. The working electrode was then changed to the silver electrode and the procedure was repeated with the potential varying between 0.00V and 0.50V. The detection limits for the analyte species were determined. The entire procedure was then repeated using both electrodes and the phthalic acid eluant. The detection limits using the phthalic acid eluant were slightly higher than those determined using the orthochlorobenzoic acid eluant.

RESULTS

The orthochlorobenzoic acid provided consistently better results than did the phthalic acid eluant. The platinum electrode was better than the silver electrode in these experiments. The response of the system to any particular analyte ion, or acid, was a function of the applied potential. Figure 1 illustrates the type of variation in response which could be seen as the potential was varied. Toward the extremes of the potential ranges, the noise increased significantly making peak identification and quantitation difficult. The best results were generally in the region 0.0V to 0.50V. Table I summarizes the data obtained from the variation in potential for the different species using the two electrodes. As can be seen, the optimum potentials do differ significantly. The possibility

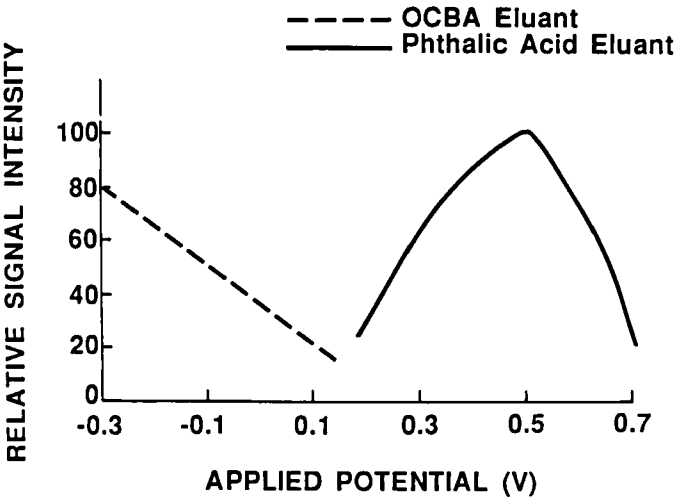

FIGURE 1: Variation of signal intensity as a function of applied potential for oxalic acid. Eluant was orthochlorobenzoic acid and a platinum electrode was used for the dotted line and the phthalic acid eluant and platinum electrode for the solid line.

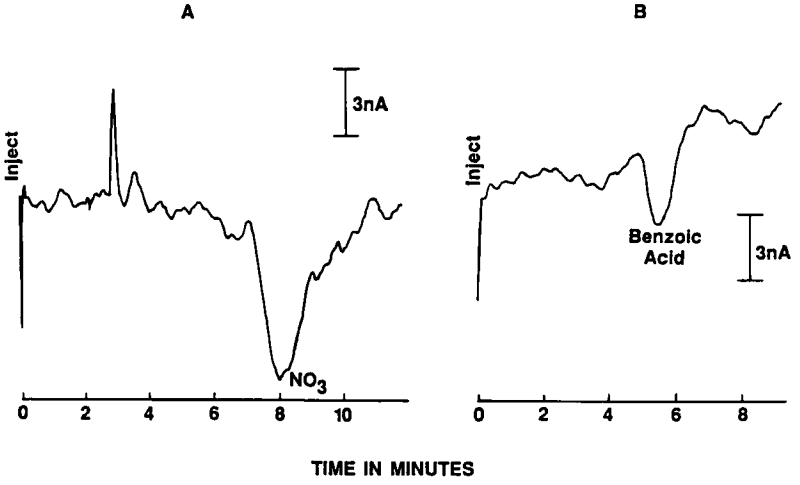

FIGURE 2: Typical chromatogram obtained using amperometric detection. Figure 2A is the nitrate ion under optimum conditions and 2B is the benzoic acid peak under optimum conditions.

arises, therefore, that the detector could be used to somewhat selectively respond to one analyte in the presence of a second analyte.

Figure 2 illustrates the types of chromatograms which were obtained in this work. Granted, these chromatograms are not necessarily the most desirable in terms of peak shape and noise, but it should be remembered that the species being observed are not, in commonly accepted theory, amenable to this type of detection.

DISCUSSION

The exact nature of the mechanism whereby these species are causing a visible change in the amperometric detector has not been determined unambiguously. The mechanism is, however, probably complex as the response differs so drastically between the species. Note in Table 1 that the EDTA does not provide a useful signal under any of the conditions tested. The lack of an EDTA signal tends to discount the theory that the eluant-analyte system is undergoing changes with respect to complexing ability of the mixture upon the electrode itself. Also, the lack of a signal for sodium sulfate indicates that a purely ionic interaction of some sort is most likely not responsible for the signal seen. It can be surmised that there is some interaction between the analyte and the electrode which alters the current carrying capacity of the system in such a way as to produce the small signals observed. It can also be assumed that the interaction is quite complex and may be the result of the constructive effect of several minor interactions producing the signal.

One other interesting observation can be made based upon the data obtained during this research. The signal obtained shifted from a positive signal to a negative signal as the potential increased while passing through a point of no discernible signal. This is again indicative of a complex mechanism between the analyte, eluant, and the electrode. Certain components of the signal, such as the inflection point, seem to be a property of the eluant, while the presence of a signal is definitely a property of the analyte.

CONCLUSION

The work reported here illustrates two key points involving ion chromatography detection. The first is that there are subtle nuances in the detection mechanisms which may be of importance when certain species are being analyzed. Secondly, stray, or unidentified, peaks present in chromatograms may be the results of a process similar to the

TABLE 1

OPTIMUM CONDITIONS FOR THE AMPEROMETRIC DETECTION OF ORGANIC ACIDS

ANALYTE	RETENTION TIME	ELUANT	APPLIED POTENTIAL	WORKING ELECTRODE	DETECTION LIMIT
Benzoic Acid	5.4 min	OCBA*	0.00V**	Pt	50 ppm
Oxalic Acid	5.6 min	PA*	0.50V	Pt	20 ppm
Sodium Nitrate	8.0 min	OCBA	0.40V	Pt	25 ppm
Phthalic Acid			NO IDENTIFIABLE PEAK		
Disodium EDTA			NO IDENTIFIABLE PEAK		
Sodium Sulfate			NO IDENTIFIABLE PEAK		

* OCBA = orthochlorobenzoic acid eluant and PA = phthalic acid eluant

** versus silver/silver chloride reference electrode

one described here and may provide useful information if used correctly, or be misleading if identified incorrectly. Again, caution and scientific integrity must be observed at all times when accounting for peaks of an unknown origin.

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