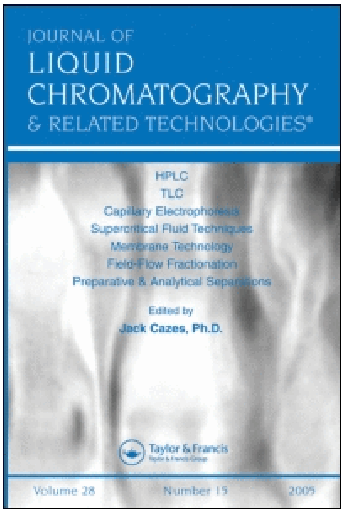
This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

The Determination of Non-Oxidizable Species Using Electrochemical Detection in Ion Chromatography

James G. Tarter[a]
[a] Department of Chemistry, North Texas State University, Denton, Texas

To cite this Article Tarter, James G.(1984) 'The Determination of Non-Oxidizable Species Using Electrochemical Detection in Ion Chromatography', Journal of Liquid Chromatography & Related Technologies, 7: 8, 1559 — 1566

To link to this Article: DOI: 10.1080/01483918408074066

URL: http://dx.doi.org/10.1080/01483918408074066

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(8), 1559-1566 (1984)

THE DETERMINATION OF NON-OXIDIZABLE SPECIES USING ELECTROCHEMICAL DETECTION IN ION CHROMATOGRAPHY

James G. Tarter
Department of Chemistry
North Texas State University
Denton, Texas 76203

ABSTRACT

The use of an electrochemical detector for the ion chromatographic detection of non-oxidizable anions such as F^-, PO_4^{-3}, NO_3^-, and SO_4^{-2} is described. The electrochemical detector is placed in line after a fiber suppressor and responds to eluent pH changes as the dissociated acids pass through the detector. The intensity of the signal is dependent on the applied potential at the cell with 0.3V being an optimum. Minimum detection limits with a 0.10 mL sample injection volume are below 0.5 ppm for F^-, Cl^-, PO_4^{-3}, NO_3^-, and SO_4^{-2}. No adverse effects on the silver working electrode have been observed.

INTRODUCTION

Ion chromatography as originally developed by Small et al. (1) used conductimetric detection to measure the ions separated by an ion exchange column. This technique uses a second column placed after the separator column to chemically suppress the conductance of the eluent by converting the buffer solution to a solution of weakly dissociated acid. This chemically suppressed ion chromatography system is generally applicable to anions with pK_a values smaller than 7. The need for dissociation restricts the analysis of such species as iodide, sulfide, thiocyanate, etc. The

0148-3919/84/0708-1559$3.50/0

electrochemical detector has been used to measure species which can be relatively easily oxidized but do not undergo sufficient dissociation for conductimetric decection (2). In practice it has been the custom to use both electrochemical and conductimetric detection to fully characterize the anions in a solution.

The work described here involves placing the electrochemical detector after the suppressor column. This arrangement causes the electrochemical detector to operate as a pH detector and thus respond to analyte ions that are not easily oxidizable. This phenomenon has been reported previously, but a thorough investigation was not undertaken (3).

EXPERIMENTAL

Equipment and Reagents

The equipment and general operating conditions used in this work are given in Table 1. All of the equipment was "as received" from the manufacturer. All operating conditions are standard conditions for the routine analysis of inorganic anions.

The standard anion solution was prepared by the appropriate dilution of 1000 ppm standard stock solutions made from reagent grade sodium salts. Distilled-deionized water was used to prepare all solutions which were introduced into the ion chromatograph including the ion chromatographic eluent.

Procedure

The normal procedure for the use of the ion chromatograph was followed with the exception that the electrochemical detector was placed after the fiber suppressor.

The pH of the effluent was measured in the following manner. The pH sensing assembly involved placing the combination pH electrode inside the barrel of a 6 mL disposable syringe. The outlet from the electrochemical detector was connected to the outlet of the disposable syringe with a female luer adapter. The pH of the solution was read manually from the pH meter display.

TABLE 1

Instrumental Parameters

Instrument:	Dionex Ion Chromatograph 10 Dionex Conductivity Detector Dionex Electrochemical Detector
Columns:	Dionex HPIC-AS3 Anion Analysis, 250mm Dionex AFS Fiber Suppressor
Eluent:	0.003 M $NaHCO_3$ + 0.0024 M Na_2CO_3
Injection Volume:	0.10 mL
Electrochemical:	0.00V to 0.45 V applied potential versus Ag/AgCl 5 nA to 100 nA full scale deflection
Conductivity:	30 μS full scale deflection
pH Meter:	Orion Research digital ionalyzer 501 Orion Lab Grade Combination pH electrode
Chart Speed:	0.5 cm/min
Standard Anion Solution:	4 ppm F^-, 4 ppm Cl^-, 20 ppm PO_4^{-3} 20 ppm NO_3^-, and 20 ppm SO_4^{-2}

RESULTS AND DISCUSSION

Figure 1 is an example of the conductivity and electrochemical chromatograms of the standard anion solution. The peaks in the conductivity chromatogram come later than the corresponding peaks in the electrochemical chromatogram due to the fact that the solution must travel through additional tubing between the two detectors. For all practical purposes, the two chromatograms are virtually indistinguishable.

The response of the electrochemical detector to nonoxidizable species can be explained based upon the changes in the eluent pH. As the eluent passes through the fiber suppressor, the cations are exchanged for hydronium ions. The eluent is converted into the weakly dissociated carbonic acid which does not liberate gas due to the pressures involved in ion chromatography. The cations which accompany the analyte ions are also exchanged producing the corresponding acid. Since all of the species routinely analyzed with conductivity detection in ion chromatography are reasonably

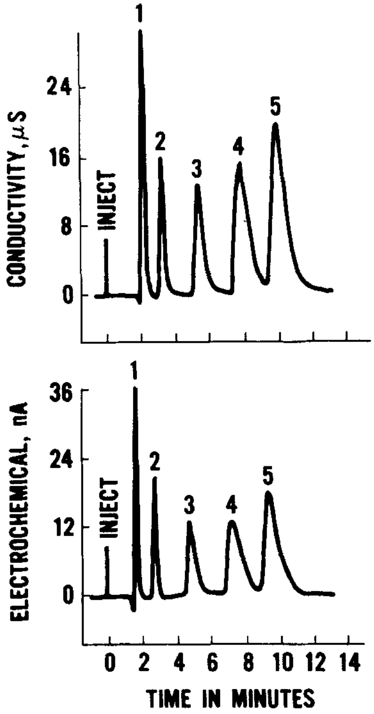


FIG. 1. Conductivity and Electrochemical Chromatograms of Standard Anion Solution. 1 = F^-, 2 = Cl^-, 3 = PO_4^{-3}, 4 = NO_3^-, and 5 = SO_4^{-2}.

well dissociated, the eluent pH will change from the background carbonic acid solution pH due to the presence of the dissociated acid. Species which are electroactive still respond to the potential applied to the cell.

The pH detector was assembled and placed in line immediately after the electrochemical detector. Figure 2 shows the electrochemical and pH chromatograms of the standard anion solution. The pH chromatogram was constructed by plotting the observed pH every 5 seconds for the 15 minutes of the chromatogram for a total of 181 data points. It is important to note that five separate pH variations are observed which correspond almost exactly to the electrochemical chromatogram.

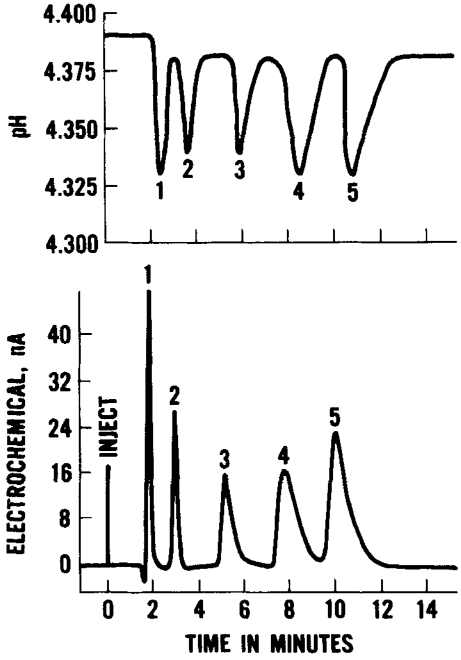


FIG. 2. Electrochemical and pH chromatograms of Standard Anion Solution. 1 = F^-, 2 = Cl^-, 3 = PO_4^{-3}, 4 = NO_3^-, and 5 = SO_4^{-2}.

The standard anion solution was chromatographed at different applied potentials. The anion peak heights were measured for five injections of the solution at each of four different applied potentials. The range of peak heights at each potential for each ion and the percent relative standard deviation (% RSD) were calculated to illustrate the reproducibility of the detector. The results from these experiments and calculations are reported in Table 2. It should be noted that the detector full scale response setting was varied to allow for peaks of sufficient height to minimize peak height measurement errors.

The following conclusions can be drawn from the data. The electrochemical detector will respond to common anions (whether oxidizable or not) at applied potentials customarily used in ion

TABLE 2

Peak Height Reproducibility*

ION		APPLIED POTENTIAL			
		0.00V	0.15V	0.30V	0.45V
F^-	range-cm	12.80-13.00	10.55-10.70	20.70-21.20	9.55-10.00
	% RSD	0.61%	0.58%	0.95%	2.35%
Cl^-	range-cm	10.05-10.15	6.50-6.60	11.70-11.90	5.15-5.50
	% RSD	0.35%	0.54%	0.70%	2.93%
PO_4^{-3}	range-cm	4.25-4.40	3.60-3.65	7.10-7.25	3.30-3.55
	% RSD	1.54%	0.76%	0.79%	3.36%
NO_3^-	range-cm	4.50-4.70	3.65-3.70	7.25-7.45	3.35-3.55
	% RSD	1.64%	1.13%	1.01%	2.60%
SO_4^{-2}	range-cm	7.35-7.45	5.10-5.20	10.05-10.20	4.65-4.90
	% RSD	0.60%	0.81%	0.56%	2.44%
Detector Full Scale Response		5nA	30nA	30nA	100nA

*Data is for five injections of same solution

chromatography using the silver electrode. The intensity of the signal is related to the magnitude of the applied potential indicating that higher applied potentials will produce increased sensitivities. As the potential nears the upper limit for the silver working electrode, the reproducibility begins to show a marked decrease. The optimum working potential appears to be approximately 0.30 V which will produce a relatively intense signal without compromising reproducibility.

Various dilutions of the standard anion solution were prepared to ascertain the range of concentrations amenable to detection using the electrochemical detector. The upper concentration limit is imposed by column overloading as is the case with conductimetric detection. Column overloading conditions vary with the anion but are apparent from the irregular peak shape

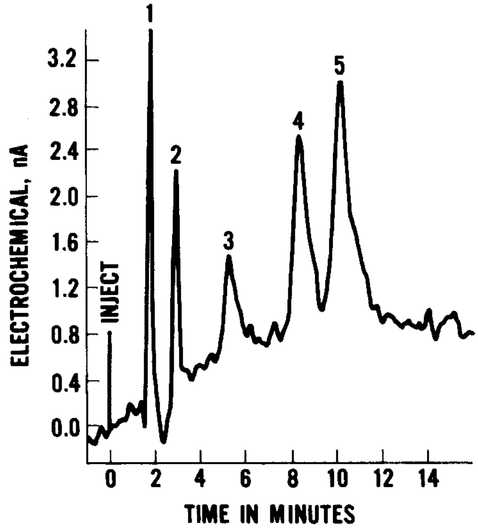


FIG. 3. Electrochemical chromatogram of dilute anion solution. Detector response 5 nA/V full scale deflection. 1 = 0.2 ppm F^-, 2 = 0.2 ppm Cl^-, 3 = 1.0 ppm PO_4^{-3}, 4 = 1.0 ppm NO_3^-, and 5 = 1.0 ppm SO_4^{-2}.

which results. This is easy to overcome simply by dilution of the sample. In general, linear response of 3 orders of magnitude can be expected depending upon column conditions and baseline stability due to pump noise. Figure 3 is the chromatogram of the diluted standard anion solution. 5.0 mL of the standard anion solution were diluted to 100.0 mL in a volumetric flask using the chromatographic eluent as the diluent. The baseline is not as stable as in Figures 1 or 2 but the peaks are still quite easily quantified. The concentrations suitable for analysis could be lowered even further with the use of either a larger injection volume or a preconcentrator column.

No adverse effects have been observed upon the silver working electrode by using this procedure. The electrode should be cleaned periodically to assist in baseline stability for solutions of low concentration, but this takes only a few minutes.

CONCLUSIONS

The use of the electrochemical detector as a pH detector provides for the use of one detector to determine the range of ionic species which normally required two detectors in the past. This should assist in simplifying ion chromatographic analysis and further extending the usefulness of this technique.

ACKNOWLEDGEMENTS

The author would like to acknowledge the financial support of the Faculty Research Fund at North Texas State University.

REFERENCES

1. Small, H., Stevens, T. S., and Bauman, W. C. Novel Ion Exchange Chromatographic Method Using Conductimetric Detection, Anal. Chem. 47, 1801, 1975.

2. Smith, F. C., Jr., and Chang, R. C. "The Practice of Ion Chromatography." John Wiley & Sons, New York, 1983, pp. 84-86.

3. Tarter, J. G. Gradient Elution Ion Chromotographic Determination of Inorganic Anions, Submitted to ANALYTICAL CHEMISTRY.